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SCS Engineers, Long Beach, CA

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Selected Biodegradation Techniques for Treatment and/or Ultimate Disposal of Organic Materials

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Organic constituents in aqueous process effluent from various industries often have properties not readily treatable by conventional biological processes. These properties include high COD/BOD ratios, low nutrient content, biocidal content, marginally degradable constituents, and a tendency toward highly variant concentrations (shock loading). For this reason, research was conducted to identify, characterize, and compare types of biological treatment processes and operational methods that successfully handle problematic organic industrial waste. The objectives of the technology comparison are to identify the most robust biological treatment techniques (applicable to the broadest range of waste classes) and to describe those treatment characteristics that specifically enhance biodegradation of organic waste. Design, performance, and economic comparisons of the studied biological treatment technologies are presented to assist waste managers and engineers in the selection of proper treatment methods. The treatment techniques studied were activated sludge, series lagoons, deep shaft aeration, and pure oxygen biological systems.

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by

SCS Engineers
Long Beach, California 90807

Contract No. 68-03-2475

Project Officer

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MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinkint water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

Organic constituents in aqueous process effluent from various industries often have properties not readily treatable by conventional biological processes. These properties include high COD/BOD ratios, low nutrient content, biocidal content, marginally degradable constituents, and a tendency toward highly variant concentrations (shock loading). For this reason, research was conducted to identify, characterize, and compare types of biological treatment processes and operational methods that successfully handle problematic organic industrial waste.

Francis T. Mayo, Director
Municipal Environmental
Research Laboratory

ABSTRACT

Organic constituents in aqueous process effluent from various industries often have properties not readily treatable by conventional biological processes. These properties include high COD/BOD ratios, low nutrient content, biocidal content, marginally degradable constituents, and a tendency toward highly variant concentrations (shock loading). For this reason, research was conducted to identify, characterize, and compare types of biological treatment processes and operational methods that successfully handle problematic organic industrial waste. The objectives of the technology comparison are to identify the most robust biological treatment techniques (applicable to the broadest range of waste classes) and to describe those treatment characteristics that specifically enhance biodegradation of organic waste. Design, performance, and economic comparisons of the studied biological treatment technologies are presented to assist waste managers and engineers in the selection of proper treatment methods.

Additional research was conducted in order to determine the removal efficiency of hazardous organic materials at three different biological treatment facilities (activated sludge, series lagoons, and deep shaft aeration). The data were used to compare influent and effluent loading of hazardous organics for removal efficiencies and the concentration of hazardous organics in the waste biological sludge. The concentration of any one hazardous organic in the waste did not exceed 2 mg/ℓ, and the majority was present in the 1-100 μg/ℓ range. The series lagoons systems demonstrated the best assimilation of the largest variety of hazardous organics. The varied biochemical reactions facilitated by each lagoon environment and extended retention period are suggested as determining factors. Analysis of biological sludges from the studied facilities indicates the tendencies of these materials to adsorb hazardous organics intact.

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CONTENTS

Page

Foreword iii
Abstract iv
Figures vii
Tables xi
Acknowledgements xviii

Section

I Introduction 1

II Conclusions and Recommendations 5

III Literature Review 10

- The Waste Stream 10
- General Waste Qualities 31
- Classes of Organic Wastes Not Amenable to Biodegradation 37
- Required Degree of Treatment 40
- Practical Applications of Biodegradation of Organic Industrial Wastes 55
- Microbial Assimilation of Organic Wastes 96

IV Site Studies 103

- Gulf Coast Waste Disposal Authority (GCWDA) 40-Acre Industrial Waste Treatment Facility, Texas City, Texas 105
- Gulf Coast Waste Disposal Authority (GCWDA) Washburn Tunnel Industrial Waste Treatment Facility, Pasadena, Texas 161
- ICI Deep Shaft Aeration Process, Paris, Ontario, Canada 204

CONTENTS (continued)

Section		Page
	• An Eastern Chemical Production Plant (UNOX) Facility	235
V	Sampling Activities	267
	• 40-Acre Facility	269
	• Washburn Tunnel Facility	282
	• Deep Shaft Facility	295
VI	Engineering and Economic Comparisons of Identified Biodegradation Techniques	305
VII	References	321
Appendices		
A.	Bibliography of pertinent literature pertaining to microbial degradation of organics	337
B.	Sampling and Analysis: Parameter and Station Selection	342
	• Selection of organic toxins for Sampling and analysis	342
	• Selection of Biological parameters for analysis	342
	• Station selection and sampling frequency	350
	• Sampling Methods	350
	• Analytical Methods	355

FIGURES

Number		Page
1	Sources of organic and inorganic waste streams from various industries	11
2	Classification of organic compounds which may occur in petrochemical waste streams	16
3	Clarification of inorganic compounds which may occur in petrochemical waste streams	18
4	Effluent characteristics: bleached kraft mill	24
5	Flow rates in coal gasification	30
6	A Rhode Island textile industry effluent profile: COD, BOD, and suspended solids versus time	33
7	Example of a deep shaft aeration plant treatment scheme	64
8	Schematic diagram of three-stage UNOX system	66
9	Two stages of anaerobic waste stabilization	74
10	Possible biological and chemical reactions in anaerobic treatment lagoon processes	76
11	Aerobic activated carbon treatment/regeneration: schematic flow diagram	85
12	GCWDA 40-Acre facility layout	106
13	Location of GCWDA 40-Acre facility	108
14	Location of industries supplying influent to 40-Acre facility	110
15	Historical representation of waste streams entering the GCWDA 40-Acre treatment facility	111
16	Anaerobic-aerobic demonstration system for determining waste treatment design at 40-Acre	126

FIGURES (continued)

Number		Page
17	GCWDA 40-Acre facility layout: schematic diagram	133
18	40-Acre distribution piping	135
19	Ashbrook mechanical surface aerator - high speed (MSAH)	137
20	COD removal as a function of loading and temperature	139
21	Relationship between BOD and COD removal	140
22	Effect of lagoon depth on COD removal and sulfide level	141
23	Effect of additional aeration on aerated stabilization effluent	143
24	Relationship of lagoon feed and effluent solids levels	144
25	Location of monitoring hardware	147
26	Maps of Houston, Texas, and vicinity	163
27	Map of Washburn Tunnel	164
28	Washburn Tunnel facility influent concentrations (ppm) monthly influent/effluent reports - 1976	181
29	Influent to Washburn Tunnel treatment plant 1976 (lbs/day)	182
30	Process flows through the GCWDA Washburn Tunnel facility	185
31	Washburn Tunnel facility cooling tower	187
32	Washburn Tunnel facility: GCWDA existing sampling stations	190
33	Washburn Tunnel facility effluent concentrations (ppm) monthly influent/effluent reports - 1976	197
34	Effluent from Washburn Tunnel treatment plant	198

FIGURES (continued)

Number		Page
35	Washburn Tunnel facility: Approximation of nutrient balance	200
36	Paris, Ontario: Regional map	206
37	Paris, Ontario: Local map	207
38	BOD loading rates	211
39	Plan view of the Deep Shaft facility	213
40	Sketch of Deep Shaft structural housing	214
41	Sealing of the Deep Shaft conduit	216
42	Paris, Ontario Deep Shaft flow diagram	218
43	Deep Shaft daily data log	222
44	Deep Shaft daily digestor data log	223
45	Schematic of wastewater flow through UNOX plant	239
46	Schematic diagram of UNOX system	241
47	Flow control and mixing in the UNOX system - overhead view	242
48	Flow diagram of a "lindox" PSA oxygen generating system	246
49	UNOX system removal efficiencies - (MLVSS used in F/M calculations)	255
50	UNOX system removal efficiencies - BOD_5 and COD vs. sludge age	256
51	UNOX system effluent quality vs. F/M ratio (MLVSS used in F/M calculations)	257
52	UNOX system effluent quality vs. sludge age	258
53	GCWDA 4-Acre Facility layout, and sampling sites	272
54	Washburn Tunnel Facility layout and sampling sites	285
55	Paris Deep-Shaft Facility	297

FIGURES (continued)

Number		Page
56	Approach to comparisons of studied technologies	307
57	Two conceptual industrial waste treatment systems utilizing primary aerobic evaluation-stabilization units	315
B-2	Location of control and outfall sediment sampling sites	351
B-3	Hypothetical fluctuation of one constituent in-plant influent-effluent	352
B-4	Composite sampler equipment	354
B-5	Grab sampler equipment	356

TABLES

Number		Page
1	Quantity of Potentially Hazardous Waste and Hazardous Constituents Generated by the Petroleum Refining Industry	14
2	Industrial Wastewater Oxygen Demand and Organic Carbon	17
3	Hazardous Wastes Generated by the Pharmaceutical Industry	20
4	Summary of Typical Types of Organic Pharmaceutical Hazardous Waste Materials	21
5	Drug Manufacturing Wastes	23
6	1972 Production by Pulp Type and Paper Grades	26
7	Typical Analysis of Ammoniacal Liquor and Still Waste	27
8	Analyses of Coke Oven Liquors by the British Coke Research Association	28
9	A Rhode Island Dyehouse Raw Waste Profile and Dyeing Cycle Components	32
10	Problem Concentrations of Tested Materials as Determined by Manometric Investigations	38
11	Biological Degradability of Aromatic Compounds	41
12	Biological Degradability of Cycloaliphatic	44
13	Biological Degradability of Aliphatic Compounds	45
14	Comparison of COD, BOD, and ThOD with Respect to Theoretical Organic Chemicals	46
15	Treatment Plant Survey Data	49
16	BPCTCA Effluent Limitations in kg/t	51

TABLES (continued)

Number		Page
17	Maximum Thirty-Day Average Effluent Limitations Guidelines: Iron and Steel Industry	53
18	Maximum Thirty-Day Average Effluent Limitations Guidelines: Textile Mills for July 1, 1977	54
19	Applications of Conventional Treatment Schemes to Various Organic Industrial Wastes as Reported in the Literature	56
20	Applications of Innovative Treatment Schemes to Various Organic Wastes as Reported in the Literature	59
21	Operating Conditions and Plant Efficiencies for Two Deep Shaft Aeration Plants	65
22	Comparisons of Process Design Conditions for the UNOX System and for Conventional Air Aeration Systems for Typical Municipal Wastewater	68
23	UNOX vs. Conventional Air Activated Sludge	69
24	Summary of UNOX System Experience with Chemical and Petrochemical Wastes	70
25	Phenol Degradation Rates in Tapered Fluidized Bed Bioreactor	73
26	Removal of Specific Organics in Anaerobic Lagoons	77
27	Data from Union Carbide Pilot and Full-Scale Studies	79
28	Construction Cost Summay Anaerobic-Aerated Stabilization System	81
29	Estimated Operating Cost Anaerobic-Aerated Stabilization System	82
30	Experimental Results on the Octanol Plant Waste Treatment by Various Processes	84
31	Carbon Addition to Activated Sludge - DuPont PACT Process	93

TABLES (continued)

Number		Page
32	List of Microorganisms Reported by Various Authors to Assimilate Recalcitrant Organic Materials	97
33	Microorganisms Known to Metabolize Organochlorine Pesticides	101
34	Characterization of Influent A	112
35	Characterization of Influent A Loading to the 40-Acre Facility	113
36	Characterization of Influent B_1	115
37	Characterization of Influent B	116
38	Characterization of Influent B Loading Values	117
39	Characterization of Influent C	118
40	Characterization of Influent C Loading Values	119
41	Characterization of Influent D	121
42	Characterization of Influent D Loading Values	122
43	Treatment Considerations at GCWDA	123
44	Systems Studied for Application at 40-Acre	124
45	Combined Influent A, B, and C Loading Values and Their Relationship to Required Nutrients	127
46	Combined Influent A, B, C, and D Loading Values and Their Relationship to Required Nutrients	128
47	Dischargers 1 and 2 Influent Monitoring Requirements	129
48	Discharger 3 Influent Monitoring Requirements	130
49	Dischargers 1, 2, and 3 Influent Limitations In Kg/day (lb/day) Effective July 1, 1977	131
50	40-Acre Basin Dimensions and Retention	134
51	Ashbrook MSAH 75/900 Characteristics	138

TABLES (continued)

Number		Page
52	GCWDA 40-Acre Operational Modes as of February 1975	146
53	40-Acre Facility: Anaerobic Lagoon	148
54	40-Acre Facility: Limited Aeration Basin Effluent Quality	149
55	Aerated Stabilization Basins F/M Ratios From 1975-1976	150
56	40-Acre Facility: Aerated Stabilization Basins (ASB) Monitoring Data (1975)	151
57	40-Acre Facility: Aerated Stabilization Basins (ASB) Monitoring Data (1976)	152
58	TWQB Daily Average Effluent Loading Discharge Limitations: 8/75-7/77, and the Corresponding Monthly 40-Acre Effluent Loading Discharge for 8/75-3/77	153
59	TWQB Effluent Loading Discharge Limitations Effective 7/1/77	154
60	Average Wastewater Constituent Removal Efficiency - May 1975 through December 1976	156
61	Major Assumptions of the Construction Cost Estimate	158
62	Construction Cost Estimate: Anaerobic-Aerated Stabilization System	159
63	Temperatures in the Gulf Coast Retion of Texas	166
64	1976 Summary - Washburn Tunnel Facility: Influent Wastes	168
65	1976 Summary - Washburn Tunnel Facility: Influent Wastes (kg/day)	170
66	1976 Influent Summary - Washburn Tunnel	173
67	1976 Influent Summary - Washburn Tunnel (kg/day)	174

TABLES (continued)

Number		Page
68	NPDES Effluent Limitations for the Washburn Treatment Facility - (Effective to kg/day (lb/day) June 30, 1977	176
69	Washburn Tunnel Facility: Averages of Reported Monthly Maximum 1976 Influents	177
70	Required Levels of Treatment to Meet 1976 NPDES Permit Effluent Limitations - Washburn Tunnel Facility	178
71	Unit Capacities: Washburn Tunnel Facility	168
72	1976 Data for Primary Effluent and Aerator	179
73	Washburn Tunnel Facility - 1976 Effluent Quality Summary	194
74	Washburn Tunnel Facility - 1976 Effluent Quality Summary	195
75	Washburn Tunnel Facility: 1976 Overall Treatment Plant Efficiency	196
76	Washburn Tunnel Facility: Estimated Construction Cost Summary	202
77	Washburn Tunnel Facility: Estimated O&M Costs - 1976	203
78	Deep Shaft Facility, Paris, Ontario: Weekday (7 Day) Operation - March 4 - July 15, 1977	209
79	Deep Shaft Facility, Paris, Ontario: May 1977 Influent Monitoring Data	210
80	Deep Shaft Facility, Paris, Ontario: Weekend Operation: March 4 - July 15, 1977	226
81	Deep Shaft Facility, Paris, Ontario: May 1977 Effluent Monitoring Data	227
82	BOD_5 Removal Efficiency	228
83	COD Removal Efficiency	229
84	Suspended Solids Removal Efficiency	230

TABLES (continued)

Number		Page
85	Paris, Ontario Deep Shaft Facility: Estimated Construction Cost Summary	233
86	Paris, Ontario Deep Shaft Facility: O&M Cost 1976	234
87	Clariflocculator	250
88	UNOX System	251
89	Plant Summary	253
90	Data on F/M Ratios and Corresponding Percent Removals as Plotted in Figure 49	259
91	Data on Sludge Age and Corresponding Percent Removals as Plotted in Figure 50	260
92	Data on F/M Ratios and Corresponding Effluent Qualities as Plotted in Figure 51	261
93	Data on Sludge Age and Corresponding Effluent Qualities as Plotted in Figure 52	262
94	Design Assumptions Utilized in Development of UNOX System Costs	264
95	UNOX Facility: Estimated Construction Costs - 1976	262
96	UNOX System: Estimated O&M Costs - 1976	266
97	Characterization of 40-Acre Wastewater and Effluent Loading in kg/day for the Sampling Period	271
98	40-Acre Facility Organic and Biological Samples Locations and Identification Designations	273
99	Results of GC Analysis of Combined Extracts of Base/Neutral and Acid Fractions Isolated for 40-Acre Samples	274
100	Results of GC/MS Analysis of 40Acre Sludge Sample: 40A-ORG-COMP-7	276
101	Results of GC and GC/MS Analysis of 40-Acre Sediment Samples	278

TABLES (continued)

Number		Page
102	Characterization of Washburn Tunnel Wastewater and Effluent Loading in kg/day for Sampling Period	283
103	Washburn Tunnel Facility Organic and Biological Sample Locations and Identification Designations	286
104	Results of GC Analysis of Combined Extracts of Base/Neutral and Acid Fractions Isolated for Washburn Tunnel Samples	288
105	Results of GC/MS Analysis of Washburn Tunnel Sludge Samples WT-ORG-COMP-S16/17/27	290
106	Results of GC and GC/MS Analyses of Washburn Tunnel Sediment Sample	291
107	Characterization of the Deep Shaft Wastewater and Effluent Loading in kg/day for the Sampling Period	296
108	Deep Shaft Facility Organic and Biological Sample Locations and Identification Designations	298
109	Results of GC and GC/MS Analyses of Deep Shaft Composite Samples	300
110	Results of GC and GC/MS Analyses of Deep Shaft Grab Samples	302
111	Specific Design, Performance and Economic Criteria for Comparing Biodegradation Technologies	308
112	Cost of Equalization Facilities	317
B-1	Potential Petrochemical Waste Products	344
B-2	Candidate Organic Toxic Constituents for Field Sampling and Laboratory Analysis	345
B-3	General Classes of Organic Toxins for Analysis in Field Samples	346
B-4	Final List of Constituents for Analysis at the Four Field Sites	347
B-5	List of Organics Analyzed by GC/MS	348

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SECTION I

INTRODUCTION

Organic constituents in aqueous process effluents from numerous types of industries often include toxic or hazardous compounds not readily removed by conventional biological treatment processes. The same characteristics which make these materials undesirable in plant discharges to receiving waters may also adversely affect the in-plant biota, resulting in reduced plant efficiencies. Nevertheless, biological treatment is an important means by which such compounds can be economically converted to less innocuous materials. For this reason, research was conducted to identify and characterize types of treatment processes or innovative treatment accessories and operational methods which are successfully handling problematic organic industrial wastes.

Section 212 of the Resource Recovery Act of 1970 (PL 91-512) required the U.S. Environmental Protection Agency (EPA) to set the groundwork for a comprehensive system of national disposal sites for elimination of hazardous wastes. In 1974, work describing the magnitude of the disposal problem and technology descriptions was completed. From the resulting reports, it became evident that treatment/disposal technology was inadequate. The Office of Solid Waste Management Programs (OSWMP) asked that the Solid and Hazardous Waste Research Laboratory (SHWRL) of the National Environmental Research Center, Cincinnati, Ohio, conduct further in-depth assessments of various disposal options. This report is the result of the study commissioned to ascertain existing and promising biological detoxification and disposal technologies.

The terms "hazardous waste" and "toxic waste" are used in this study according to the scope of investigation and the professional judgment of SCS Engineers. The definitions developed for use in this report do not necessarily reflect EPA definitions, and they may or may not be in agreement with uses in federal legislation or private industry. This study is purposely focused upon waste materials potentially biocidal, carcinogenic, mutagenic, or bioaccumulative. Materials may, therefore, be excluded which present explosion or corrosion hazards in bulk, but are not considered biologically active as described by the Federal Registry of Toxic Effects of Chemical Substances.

During the execution of this study, emphasis was placed upon biological treatment technologies which are:

- Treating a wide range of classes of synthetic or toxic organic compounds
- Processing toxic compounds without resulting synergenic reactions and biological metabolites which would present an equal or enhanced potential for adverse environmental impact
- Being utilized on a large-pilot or full-scale basis. Technologies which were demonstrated on a bench scale only are not reported, except where the process showed exceptional promise for future development.
- Minimizing operating and environmental costs. The system must be cost-effective and free of secondary problems such as air pollution or excessive sludge handling/disposal requirements.

The work reported herein proceeded in consecutive steps. Initially, a data base and literature search was conducted to describe the present treatment problem and prepare an inventory of types and locations of innovative biological treatment technologies presently developed and in use. The results of this effort comprise Section III of this report. After information was assembled on candidate study sites, four (4) locations were selected for in-depth analysis. These sites included a large-scale activated sludge plant, lagoon system, a Deep Shaft pilot facility, and a UNOX pure oxygen plant. Three of the plants are treating industrial effluents exclusively; the Deep Shaft facility processes a 70:30 industrial/municipal raw influent. The plants were selected to represent the following specific process units or operational methodologies which enhance biodegradation processes:

> Intensive Aeration. Use of aeration technology to promote a high level of dissolved oxygen in the waste flow, resulting in higher rates of chemical and biological oxidation.
>
> Nutrient Addition. Industrial wastes are often "unbalanced" in the nutritional requirements of microorganisms. Addition of nitrogen and/or phosphorus, for example, has been effective in increasing biodegradation rates.

Biological Seeding. The application of known species to provide a seed for microbial populations has been made easier through the development of especially manufactured dried bacterial cultures. Species of bacteria can be selectively produced which demonstrate high rates of degradation for the particular waste involved.

Substrate Alteration. Chemical pretreatment of wastes prior to introduction into biological waste treatment systems can be a valuable means of promoting rapid biodegradation. This technique would be particularly important in the neutralization of toxins.

Growth Phase Manipulation. Innovative sludge recycling and clarification techniques may be used to optimize the food-to-microorganism ratio and maximize the metabolism rates.

Temperature Control. Biochemical reactions are temperature-dependent. Higher rates of metabolism have been associated with higher temperatures. Techniques which use temperature control for enhancing metabolism were studied.

Deep-Shaft Aeration. Oxygen transfer system comprised of a 90- to 245-m (300- to 600-ft) shaft vertically partitioned into downflow and upflow sections. Increased pressure with depth coupled with air injection allows increased oxygen transfer efficiencies to the point where biodegradability of the substrate is considered the limiting factor.

During the execution of the site studies, the field team was charged with gathering information and making observations concerning the following major topics:

- The types of wastes that are and are not physically or chemically amenable to treatment through biodegradation.
- Process design and influence of waste characteristics on the biological assimilative capacity at each site studied.
- The impact of any process effluents upon the indigenous biota when data is available.
- Efficiencies and costs incurred by site owners utilizing biodegradation techniques and future economics of the technology.

- Potential for site design changes at existing site facilities which will utilize and encourage accelerated biodegradation of industrial and hazardous organic wastes.

The results of these field investigations are reported in Section IV.

During the execution of the initial field studies, it became apparent to the contractor that insufficient data existed in treatment plant files and elsewhere to properly describe the presence and fate of specific organic constituents of interest. As expected, different quantities and types of information were available at each of the four plants. Gross measurements of organic materials such as the Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), and Total Organic Carbon (TOC) tests are of little value in situations where an evaluation of specific problematic compounds is required. For these reasons, chemical and biological sampling was instituted at three sites. A detailed sampling plan was prepared to characterize the inputs and outputs of specific organic toxins using gas/liquid chromatography and mass spectrometry. Biological samplings were also obtained to determine the characteristics of in-plant biota. The results of this work are presented in Section V.

Section VI of this report utilizes the information assembled in the previous sections to establish an engineering and economic comparison of biological treatment technologies for organic industrial process effluents. The goal of this exercise is to guide the EPA and U.S. industries in selecting treatment processes and comparing biological systems with chemical or physical/chemical treatment approaches. Comparative criteria include overall efficiency, operational and maintenance costs, capital and construction costs, ability to treat a wide spectrum of classes of organic compounds, susceptibility to shock loading or climatological fluctuations, and minimization of adverse environmental impact.

SECTION II

CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations based on the field observations and analytical results, as well as background information gathered during the extensive literature review, are presented here in association with the project goals discussed in the following sections.

The first goal involved the evaluation of treatment capabilities of biodegradation as applied to problematic wastes. The following was noted:

- The advantage of biological treatment schemes lies primarily in the degree to which such systems are acclimated to removing residual dissolved or colloidal organic contaminants.

- Treatability of general classes or organic constituents varies greatly and depends upon the biological system applied. For example, in short retention/high aeration systems recalcitrant materials may be removed by stripping into the air. In systems retaining large amounts of solids, in-plant digestion may result in the release of metabolites into the effluent wastestreams.

- Biological treatment is a significant technique for permanently mineralizing materials that are moderately biodegradable. Broad applications must be limited to situations where shock loading is controlled, certain extremely biocidal constituents are avoided, retention time is high, influents are completely mixed, and concentrated wastes are diluted.

The second goal involved the identification and description of specific wastes being successfully or unsuccessfully treated. The following was noted:

- Treatment of 35 organic compounds by a large series lagoon system resulted in a significant reduction of all compounds except fluorene, which was found to be resistant to biodegradation. Phenols, cresols, and polycyclic aromatic hydrocarbons were present in high levels in sludges compared to influent-effluent concentrations. This was attributed to the accumulation of these materials as metabolites of polymers and other complex materials in sludges.

- An evaluation of degradation of 35 organic compounds by a large, activated sludge system treating industrial wastes indicated that phenol, 1,2-diphenyl-hydrazine, and benzidine were resistant to degradation. Phenol was present in the influent with a concentration of 43 μg/l. Both aliphatic hydrocarbons and monocyclic aromatics were detected in high concentrations (2 to 5 mg/l) in the waste sludges in relation to other sludges examined.

- Biodegradability of textile chemicals indicated that most materials were only marginally amenable to conventional biological treatment and degrade very slowly. Most dyes showed little change during 5-day BOD tests, and there was little color change after 30 days. Under certain conditions, sulfur compounds were reduced to sulfides or anaerobically metabolized to form thiols by bacteria in waste treatment systems, resulting in odor problems. Some problematic organic chemicals, such as low molecular weight acids and alcohols difficult to degrade aerobically, degrade anaerobically. The blending of domestic sewage with industrial wastes can result in an improved nutrient balance and provide for concentrated industrial wastes dilution.

The third goal involved observation of any relationships between wastes and indigenous plant biota (toxic or beneficial). The following was noted:

- The flora of industrial waste treatment systems was found to have qualities and quantities similar to domestic wastewater treatment systems flora.

- During warmer months or under warm-waste conditions, biological systems may be plagued by thermophilic bacteria. Such populations are unstable and can occasionally cause poor settling in secondary clarifiers.

- Nutrient concentrations in the recycled and wasted sludges of treatment facilities should be evaluated along with influent-effluent concentrations to provide a complete picture of the balance of such materials in relation to carbonaceous substrates. At the plants studied, nutrient additions are based on the detection of trace amounts in the aqueous plant effluents. Reduction in costs for chemicals may be achieved by monitoring nutrients in secondary sludge.

The fourth goal involved an estimation of the time required to effect efficient decomposition of the organic materials. The following was noted:

- Based on the observations reported herein, the biodegradation of problematic, or hazardous organics requires a longer retention period in a biological system than required for the reduction of the Biological Oxygen Demand (BOD). Series lagoon systems are the only waste treatment option providing prolonged retention periods (>1 day) necessary for stabilization of recalcitrant organics.

The fifth goal involved an evaluation of organic wastes in treatment facility effluents, including waste accumulations in sludges. The following was noted:

- The majority of organic compounds evaluated were present in the waste streams in the parts-per-billion range of concentration. Concentrations were below toxic or inhibitory levels, a key factor in efficient biological assimilation of wastes.

- Marginally degradable organics may be removed by biological systems if the mixed liquor suspended solids are maintained sufficiently high. Under such conditions, compounds have been observed to adsorb onto the biological solids and are removed by subsequent clarification. Some of these compounds can generate secondary sludge disposal problems.

- Sludges and the sediments of receiving waters appear to be sinks for the same types of organic compounds observed in waste stream.

The sixth goal involved conducting engineering and economic comparisons and evaluations of studied technologies. The following was noted:

- Series lagoon systems can provide high system flexibility, e.g., a variant of options for waste flow patterns. Techniques for returning settled biomass to aerated stabilization lagoons should be considered for series lagoon systems to include advantages of activated sludge systems.

- Additional development of pretreatment methods for reducing the impact of varying waste stream characteristics (toxic or inhibitory effects) on biological treatment can be applied more widely to industrial wastes.

- Biological seeding is only advisable under special waste conditions. Continuous seeding must be conducted to maintain a viable degrading population where adverse environmental conditions, other microbial predators, or excessive washout occurs. The cost of continuous additions of large volumes under such circumstances may be noncompetitive with alternative treatment methods. An effective alternative to seeding involves allowing for acclimation to low concentrations of a waste before increasing loadings.

- In certain cases, activated carbon addition can be a useful and cost-effective method of improving the efficiency of existing industrial waste treatment facilities. The effectiveness of the technique is primarily due to surface-concentrating effects in systems of dilute waste concentrations. The carbon can also adsorb toxins, thereby reducing their concentrations to levels where they are not biologically inhibiting. Additional research efforts should concentrate on effective techniques for regenerating the spent carbon.

- Additional research and development should encourage practical applications of optimal feedback control systems in industrial waste treatment plants. Automation of critical operational steps can improve the response to fluctuating influent characteristics.

- The fundamental objectives of innovative biological treatment usually involve:

  - Enhanced contact between wastes and microbial cells
  - Enhanced oxygen transfer to the microbial cells
  - Minimization of toxic effects.

Additional research is necessary to develop ways of enhancing contact between wastes and microbial cells without generating demand for additional treatment unit volumes, and also for the following:

- To ease the burden on biological treatment, raw process discharges should be segregated for possible chemical recovery, incineration, stabilization, and other processing options.

- Automated systems should be provided to divert hydraulic or organic overloadings to spill basins.

- Proper pretreatment, the use of surge tanks or lagoons, and process control and housekeeping at source plants can have a significant impact on treatment plant stability. The inclusion of surge capacity can reduce the problem of solids overflow from primary and secondary clarifiers.

- Criteria based on design, performance, and economic considerations were defined and evaluated to select series lagoon systems as the most robust technology for application to general classes of industrial wastes. Both pure oxygen and deep shaft systems were judged to be superior from a design standpoint. Series lagoons were judged to have the best performance, and were also judged favorably based on economic considerations.

- Deep Shaft technology has been found to be average or better than average according to all cost criteria except where construction costs and cost per unit of waste removed are concerned. The higher removal costs are based upon limited information about the application of the new technology, and it is anticipated that future industrial installations will prove the technology to be extremely competitive. Removal costs expressed as dollars per kg of BOD for other technologies were $0.11 for series lagoons, $0.55 for the UNOX systems, and $0.22 for the activated sludge facility.

SECTION III

LITERATURE REVIEW

THE WASTE STREAM

The production and discharge of industrial and hazardous wastes have increased substantially during the last six decades. The growth of major industrial centers in the United States has been paralleled by increases in volume production of organic solids in refinery and other chemical plant effluents. Each year 1.8×10^9 t (2.0×10^9 tons) of hazardous materials and 9.07×10^7 t (1.0×10^8 tons) of organic and inorganic waste by-products are produced by U.S. industries. About 10 percent, or 9.1×10^6 t (1.0×10^7 tons) of this annual waste load is nonradioactive, organic and inorganic hazardous materials (25). Based upon approximate waste production rate, roughly 5 percent of overall production, the petrochemical industry alone produces approximately 3.5×10^6 t/yr (3.9×10^6 tons/yr) of organic and inorganic hazardous wastes, approximately 2.1×10^6 t (2.3×10^6 tons) organic.

Waste streams composed primarily of organic constituents are candidates for biological treatment. As shown in Figure 1, organic-rich wastes can originate from five major industries. The petroleum refining and organic chemical and synthetics industries are both dependent upon various sources or derivatives of domestic or imported crude oils. The third industry depends upon cellulose resources and the milling of pulp and fiber into wood and paper products. Products of the fourth industry (coal conversion and steel milling) include gases, oils, and coke for use in coke and steel production. Textile processing is the fifth industry.

The quantity of hazardous organic constituents in the waste streams from these and other U.S. industries represents about 60 percent of the total hazardous waste loading (25). Based on an estimate of 9.1×10^6 t/yr (1.0×10^7 tons/yr), the organic components then represent 5.4×10^6 t/yr (6.0×10^6 tons/yr).

Growth of the wood, coal, and petrochemical industries and modifications in production techniques have caused changes in the amounts of wastes generated. These fluctuations, coupled with simultaneous changes in the availability of raw materials, waste product reuse, and consumer demand, make it difficult to predict trends in effluent qualities. Total tonnage of product or waste production for one industry may be low in comparison to

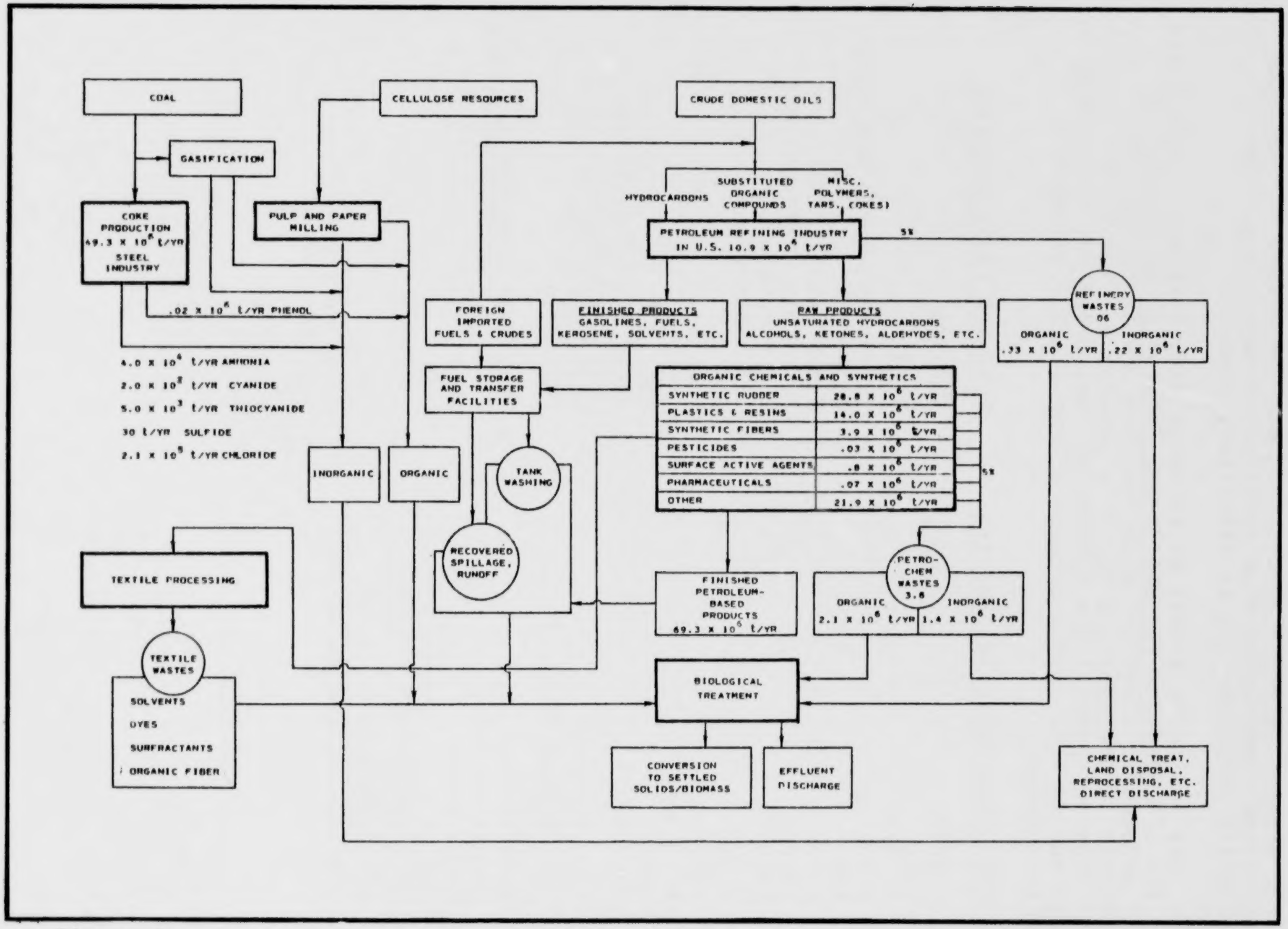
COAL
GASIFICATION
COKE PRODUCTION 49.3 X 10^6 t/YR STEEL INDUSTRY
CELLULOSE RESOURCES
PULP AND PAPER MILLING
.02 X 10^6 t/YR PHENOL
4.0 X 10^4 t/YR AMMONIA
2.0 X 10^2 t/YR CYANIDE
5.0 X 10^3 t/YR THIOCYANIDE
30 t/YR SULFIDE
2.1 X 10^5 t/YR CHLORIDE
INORGANIC
ORGANIC
CRUDE DOMESTIC OILS
HYDROCARBONS
SUBSTITUTED ORGANIC COMPOUNDS
MISC. POLYMERS, TARS, COKES)
PETROLEUM REFINING INDUSTRY IN U.S. 10.9 X 10^6 t/YR
5%
FOREIGN IMPORTED FUELS & CRUDES
FINISHED PRODUCTS GASOLINES, FUELS, KEROSENE, SOLVENTS, ETC.
RAW PRODUCTS UNSATURATED HYDROCARBONS ALCOHOLS, KETONES, ALDEHYDES, ETC.
REFINERY WASTES 06
ORGANIC .33 X 10^6 t/YR
INORGANIC .22 X 10^6 t/YR
FUEL STORAGE AND TRANSFER FACILITIES
TANK WASHING
RECOVERED SPILLAGE, RUNOFF
ORGANIC CHEMICALS AND SYNTHETICS
SYNTHETIC RUBBER 28.8 X 10^6 t/YR
PLASTICS & RESINS 14.0 X 10^6 t/YR
SYNTHETIC FIBERS 3.9 X 10^6 t/YR
PESTICIDES .03 X 10^6 t/YR
SURFACE ACTIVE AGENTS .8 X 10^6 t/YR
PHARMACEUTICALS .07 X 10^6 t/YR
OTHER 21.9 X 10^6 t/YR
5%
PETRO-CHEM WASTES 3.8
ORGANIC 2.1 X 10^6 t/YR
INORGANIC 1.4 X 10^6 t/YR
FINISHED PETROLEUM-BASED PRODUCTS 69.3 X 10^6 t/YR
TEXTILE PROCESSING
TEXTILE WASTES
SOLVENTS
DYES
SURFRACTANTS
ORGANIC FIBER
BIOLOGICAL TREATMENT
CONVERSION TO SETTLED SOLIDS/BIOMASS
EFFLUENT DISCHARGE
CHEMICAL TREAT, LAND DISPOSAL, REPROCESSING, ETC. DIRECT DISCHARGE

Figure 1. Sources of organic and inorganic waste streams from various industries.

other organic material processors, but the amount of hazardous constituents emanating from certain processes, e.g., the pesticide industry, may be relatively high.

The following groups of waste-related parameters were cited in the EPA Handbook for Monitoring Industrial Wastewater (8). The parameters cited for each industry are those for which effluent limitations are set on a general and individual basis. The organic chemical and synthetics industries are considered together in this review because of the similar effluent constituents.

Petroleum Refining Industry

- Ammonia
- BOD_5
- Chloride
- Chromium
- COD
- Color
- Copper
- Cyanide
- Iron
- Lead
- Mercaptans
- Nitrogen
- Odor
- Oil, total
- pH
- Phenol
- Phosphorus, total
- Sulfate
- Sulfide
- Suspended solids
- Temperature
- TOC
- Total dissolved solids
- Toxicity
- Turbidity
- Volatile suspended solids
- Zinc

Steel Industry

- Ammonia
- Chloride
- Chromium
- Cyanide
- Iron
- Oil and grease
- pH
- Phenol
- Sulfate
- Suspended solids
- Temperature
- Tin
- Zinc

Pulp and Paper Industry

- Ammonia
- BOD_5
- COD
- Coliforms, total and fecal
- Color
- Heavy metals
- Nutrients (nitrogen and phosphorus)
- Oil and grease
- pH
- Phenols
- Sulfite
- TOC
- Total dissolved solids
- Total suspended solids
- Toxic materials
- Turbidity

Textile Mill Products Industry

- Alkalinity
- BOD_5
- Chromium
- COD
- Color
- Heavy metals
- Oil and grease
- pH
- Phenolics
- Sulfides
- Suspended solids
- Temperature
- Total dissolved solids
- Toxic materials

Organic Chemicals and Synthetics Industry

- BOD_5
- Chlorinated benzenoids and PNA's
- Chloride, organic
- COD
- Cyanides
- Heavy metals
- Nitrogen, total
- Oil, free-floating
- pH
- Phenol
- Phosphorus, total
- Other pollutants
- Total dissolved solids
- Total suspended solids
- Sulphates, mercaptans
- TOC
- Zinc

Petroleum Refining

In the literature, aqueous effluents from petroleum refineries are not always well differentiated from solid waste components. Treatment options will vary depending upon the percent water. Table 1 (136) shows the quantities of potentially hazardous waste and hazardous constituents generated each year by the United States petroleum refining industry. In addition to the trace elements shown, the oil and phenol fractions may be further differentiated into polynuclear aromatics, specific phenolic compounds, and various substituted and nonsubstituted hydrocarbons. These materials form the major portion of those refining waste compounds believed to be carcinogenic. Hydrocarbons may be introduced into aqueous process streams in primary distillation processes, where the crude feed stocks are entering the system. The three types of saturated hydrocarbons- aliphatics, aromatics, and cyclic aliphatics that may be found, differ in volatility and amenability to biological degradation. Unsaturated hydrocarbons include the olefinic series (alkenes). These compounds are more soluble and reactive than saturated hydrocarbons and reactive in the plant process and waste streams. Mixed aliphatic-aromatic compounds can also be expected in petroleum refinery effluents (50).

Organic Chemicals and Synthetics

The petrochemical industry uses petroleum components for the manufacturing of polymers, fibers, or complex organics resulting from chemical synthesis. Specific industries specialize in synthetic rubber, plastics and resins, synthetic fibers (nylon, etc.), surface-active agents (dispersants, soaps), pesticides, and other miscellaneous petroleum-derived products. It is estimated that the total petroleum-based production yields 6.93 x 10^7 t/yr (7.6 x 10^7 tons/yr) (50).

TABLE 1. QUANTITY OF POTENTIALLY HAZARDOUS WASTE AND HAZARDOUS CONSTITUENTS GENERATED BY THE PETROLEUM REFINING INDUSTRY (t/yr - 1974) (136)

Total potentially hazardous wastes	wet	1756633.3206
	dry	624540.9959
Total hazardous constituents (dry basis)		110884.7286
	Phenol	5.3367
	CN	1.07532
	Se	1.50562
	As	2.07518
	Hg	.44461
	Be	.07633
	V	19.8619
	Cr	87.782
	Co	2.7087
	Ni	23.4657
	Cu	22.0568
	Zn	78.177
	Ag	.52749
	Cd	.19363
	Pb	14.5644
	Mo	2.1343
	NH_4	4.9334
	PNA	.1126
	F	811.93
	Oil	109,806

The organic waste-stream components of organic chemical and synthetic processing are extremely complex. Substitution and synthesis reactions involving first-generation petroleum products are supplemented or catalyzed by a variety of metals, halogens, nonpetroleum-based organics, and intermediate substituted chemicals. Complex catalysts are also used for enhancing such reactions. In spite of the great variety of compounds manufactured, only 100 chemical products represent 90 percent of the total sales of organic chemical intermediates (144).

The first generation petroleum products are the alkanes, alkenes, aromatics, olefins, and paraffins, which are derived from initial refining of crude petroleums (Figure 2). Intermediate substituted organics are derived from chemical oxydation, substitution or addition reactions of first generation products with other organic or inorganic chemicals. These reactions form ethylene oxide, carboxylic acids, and various organic acids. Chemicals classified as organic intermediates may be market products or temporary synthesis steps in the production of final products such as synthetic detergent bases, plastics and resins, fibers, or solvents (107).

Figure 2 shows the types of organic compounds that may be present in waste streams of petrochemical product manufacturers. As indicated, practically every organic intermediate product may appear. However, the concentrations of each constituent in the waste stream will vary, depending upon solubility, volatility, and proximity to spills or contaminating process streams. Additional factors affecting the concentration of organic chemicals in aqueous petrochemical wastes include the age and condition of reaction vessels and transfer piping, in-plant maintenance and spill prevention, and the efficiency of energy and mass transfers during the chemical reaction. Table 2 shows BOD and COD values for a number of chemical industries. Note the high level of COD compared to BOD.

The metal and nonmetal inorganic compounds in petrochemical production waste streams can have significant impact upon biological treatment processes. Cyanide, chromium, and other trace constituents can, at certain concentrations, inhibit metabolism or severely disrupt cell membranes (88).

Metals appearing in process effluents are primarily unrecovered catalytic materials, corrosion products, inorganic raw material residues, and additives in association with the organic waste residues (Figure 3). Processes such as catalytic reforming, polymerization, alkylation, and dehydrogenation utilize metal catalysts comprised of aluminum, molybdenum, iron, chromium, or platinum (50). Other sources of metals include gas purification (copper), cooling tower sludges, and cooling waters (zinc, aluminum, and others). Zinc, chromium, or copper compounds are also introduced into aqueous process streams to control corrosion and prevent biological growth.

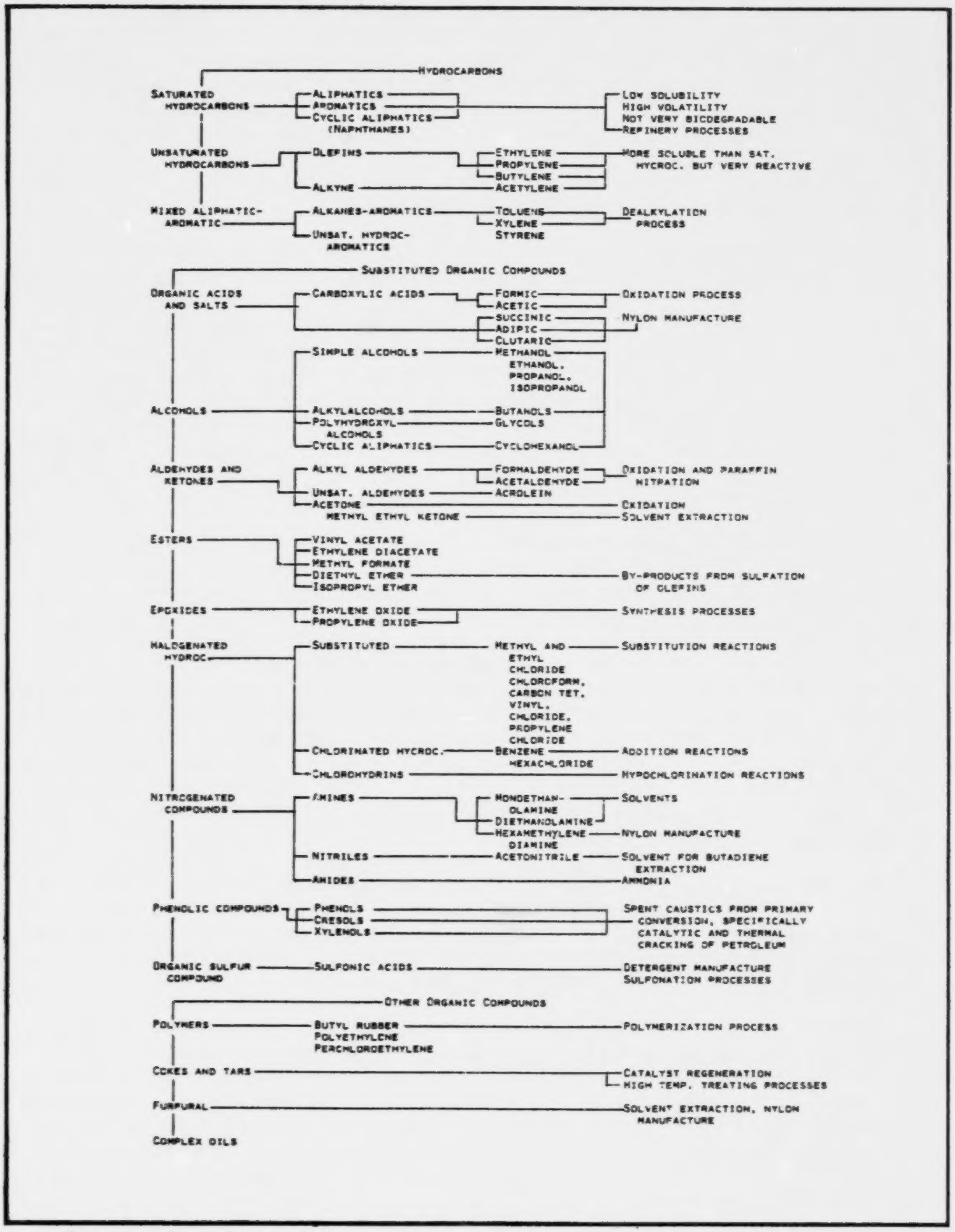
HYDROCARBONS
SATURATED HYDROCARBONS
ALIPHATICS
AROMATICS
CYCLIC ALIPHATICS (NAPHTHANES)
LOW SOLUBILITY
HIGH VOLATILITY
NOT VERY BIODEGRADABLE
REFINERY PROCESSES
UNSATURATED HYDROCARBONS
OLEFINS
ALKYNE
ETHYLENE
PROPYLENE
BUTYLENE
ACETYLENE
MORE SOLUBLE THAN SAT. HYCROC. BUT VERY REACTIVE
MIXED ALIPHATIC-AROMATIC
ALKANES-AROMATICS
UNSAT. HYDROC-AROMATICS
TOLUENE
XYLENE
STYRENE
DEALKYLATION PROCESS
SUBSTITUTED ORGANIC COMPOUNDS
ORGANIC ACIDS AND SALTS
CARBOXYLIC ACIDS
FORMIC
ACETIC
SUCCINIC
ADIPIC
GLUTARIC
OXIDATION PROCESS
NYLON MANUFACTURE
ALCOHOLS
SIMPLE ALCOHOLS
ALKYLALCOHOLS
POLYHYDROXYL ALCOHOLS
CYCLIC ALIPHATICS
METHANOL ETHANOL, PROPANOL, ISOPROPANOL
BUTANOLS
GLYCOLS
CYCLOHEXANOL
ALDEHYDES AND KETONES
ALKYL ALDEHYDES
UNSAT. ALDEHYDES
ACETONE
METHYL ETHYL KETONE
FORMALDEHYDE
ACETALDEHYDE
ACROLEIN
OXIDATION AND PARAFFIN NITRATION
OXIDATION
SOLVENT EXTRACTION
ESTERS
VINYL ACETATE
ETHYLENE DIACETATE
METHYL FORMATE
DIETHYL ETHER
ISOPROPYL ETHER
BY-PRODUCTS FROM SULFATION OF OLEFINS
EPOXIDES
ETHYLENE OXIDE
PROPYLENE OXIDE
SYNTHESIS PROCESSES
HALOGENATED HYDROC.
SUBSTITUTED
CHLORINATED HYCROC.
CHLOROHYDRINS
METHYL AND ETHYL CHLORIDE CHLOROFORM, CARBON TET. VINYL. CHLORIDE, PROPYLENE CHLORIDE
BENZENE HEXACHLORIDE
SUBSTITUTION REACTIONS
ADDITION REACTIONS
HYPOCHLORINATION REACTIONS
NITROGENATED COMPOUNDS
AMINES
NITRILES
AMIDES
MONOETHANOLAMINE
DIETHANOLAMINE
HEXAMETHYLENE DIAMINE
ACETONITRILE
SOLVENTS
NYLON MANUFACTURE
SOLVENT FOR BUTADIENE EXTRACTION
AMMONIA
PHENOLIC COMPOUNDS
PHENOLS
CRESOLS
XYLENOLS
SPENT CAUSTICS FROM PRIMARY CONVERSION, SPECIFICALLY CATALYTIC AND THERMAL CRACKING OF PETROLEUM
ORGANIC SULFUR COMPOUND
SULFONIC ACIDS
DETERGENT MANUFACTURE
SULFONATION PROCESSES
OTHER ORGANIC COMPOUNDS
POLYMERS
BUTYL RUBBER
POLYETHYLENE
PERCHLOROETHYLENE
POLYMERIZATION PROCESS
COKES AND TARS
CATALYST REGENERATION
HIGH TEMP. TREATING PROCESSES
FURFURAL
SOLVENT EXTRACTION, NYLON MANUFACTURE
COMPLEX OILS

Figure 2. Classification of organic compounds which may occur in petrochemical waste streams.

TABLE 2. INDUSTRIAL WASTEWATER OXYGEN DEMAND AND ORGANIC CARBON (46)

Type of Waste	BOD_5 (mg/ℓ)	COD (mg/ℓ)	TOC (mg/ℓ)	BOD:TOC	COD:TOC
Chemical*	--	4,260	640	--	6.65
Chemical*	--	2,440	370	--	6.60
Chemical*	--	2,690	420	--	6.40
Chemical	--	576	122	--	4.72
Chemical	24,000	41,300	9,500	2.53	4.35
Chemical-refinery	--	580	160	--	3.62
Petrochemical	--	3,340	900	--	3.32
Chemical	850	1,900	580	1.47	3.28
Chemical	700	1,400	450	1.55	3.12
Chemical	8,000	17,500	5,800	1.38	3.02
Chemical	60,700	78,000	26,000	2.34	3.00
Chemical	62,000	143,000	48,140	1.28	2.96
Chemical	--	165,000	58,000	--	2.84
Chemical	9,700	15,000	5,500	1.76	2.72
Nylon polymer	--	23,400	8,800	--	2.70
Petrochemical	--	--	--	--	2.70
Nylon polymer	--	112,600	44,000	--	2.50
Olefin processing	--	321	133	--	2.40
Butadiene processing	--	359	156	--	2.30
Chemical	--	350,000	160,000	--	2.19
Synthetic rubber	--	192	110	--	1.75

*High concentration of sulfides and thiosulfates.

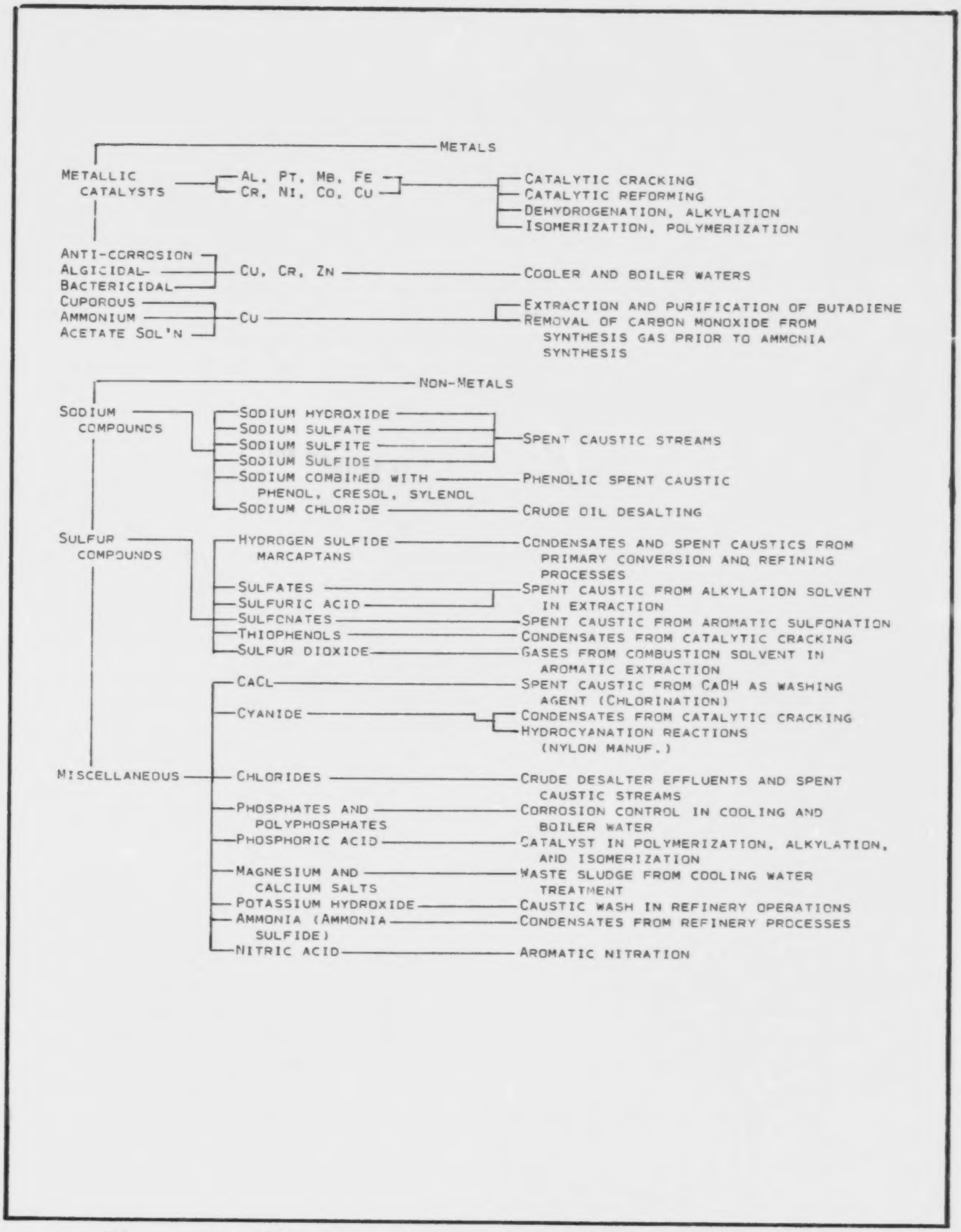
METALS
METALLIC CATALYSTS
AL, PT, MB, FE
CR, NI, CO, CU
CATALYTIC CRACKING
CATALYTIC REFORMING
DEHYDROGENATION, ALKYLATION
ISOMERIZATION, POLYMERIZATION
ANTI-CORROSION
ALGICIDAL
BACTERICIDAL
CU, CR, ZN
COOLER AND BOILER WATERS
CUPOROUS
AMMONIUM
ACETATE SOL'N
CU
EXTRACTION AND PURIFICATION OF BUTADIENE
REMOVAL OF CARBON MONOXIDE FROM SYNTHESIS GAS PRIOR TO AMMONIA SYNTHESIS
NON-METALS
SODIUM COMPOUNDS
SODIUM HYDROXIDE
SODIUM SULFATE
SODIUM SULFITE
SODIUM SULFIDE
SPENT CAUSTIC STREAMS
SODIUM COMBINED WITH PHENOL, CRESOL, SYLENOL
PHENOLIC SPENT CAUSTIC
SODIUM CHLORIDE
CRUDE OIL DESALTING
SULFUR COMPOUNDS
HYDROGEN SULFIDE MARCAPTANS
CONDENSATES AND SPENT CAUSTICS FROM PRIMARY CONVERSION AND REFINING PROCESSES
SULFATES
SULFURIC ACID
SPENT CAUSTIC FROM ALKYLATION SOLVENT IN EXTRACTION
SULFONATES
SPENT CAUSTIC FROM AROMATIC SULFONATION
THIOPHENOLS
CONDENSATES FROM CATALYTIC CRACKING
SULFUR DIOXIDE
GASES FROM COMBUSTION SOLVENT IN AROMATIC EXTRACTION
MISCELLANEOUS
CACL
SPENT CAUSTIC FROM CAOH AS WASHING AGENT (CHLORINATION)
CYANIDE
CONDENSATES FROM CATALYTIC CRACKING
HYDROCYANATION REACTIONS (NYLON MANUF.)
CHLORIDES
CRUDE DESALTER EFFLUENTS AND SPENT CAUSTIC STREAMS
PHOSPHATES AND POLYPHOSPHATES
CORROSION CONTROL IN COOLING AND BOILER WATER
PHOSPHORIC ACID
CATALYST IN POLYMERIZATION, ALKYLATION, AND ISOMERIZATION
MAGNESIUM AND CALCIUM SALTS
WASTE SLUDGE FROM COOLING WATER TREATMENT
POTASSIUM HYDROXIDE
CAUSTIC WASH IN REFINERY OPERATIONS
AMMONIA (AMMONIA SULFIDE)
CONDENSATES FROM REFINERY PROCESSES
NITRIC ACID
AROMATIC NITRATION

Figure 3. Clarification of inorganic compounds which may occur in petrochemical waste streams.

Nonmetal constituents from petrochemical production include salts, chlorides, cyanide, and phosphorous, nitrogenous and sulfur compounds (Figure 3). Sodium salts, which may react chemically with other inorganic or organic chemicals, originate primarily from caustic wash streams. Sulfur compounds are important because, in certain forms, they can be toxic to the receiving biota or can generate odor problems. Hydrogen sulfide, thiols, sulfates and sulfonates may be produced in extraction processes, caustic washings, and catalytic cracking or conversion processes. Under appropriate environmental conditions, sulfur compounds are reduced to sulfides or anaerobically metabolized to form thiols by bacteria in waste treatment systems. The generation of these compounds can create severe operational and odor problems for the treatment plant.

The pharmaceuticals industry is a significant contributor of organic hazardous wastes to the organic chemicals waste stream. The types of waste and applied treatment methods require special consideration because of the biocidal potential of some constituents. In addition, certain pharmaceutical waste products may be extremely resistant to biodegradation by conventional means.

An EPA contractor (6) has estimated that a total of 73,755 t (81,300 tons) (wet basis) of hazardous wastes will be generated by the pharmaceuticals industry in 1977 (Table 3). Except for 225 t/yr (248 tons/yr) of heavy metal, most of these materials are organic compounds. A summary of the typical organic pharmaceutical hazardous waste materials to be found in process effluents is shown in Table 4.

The largest tonnage of process wastes comes from the production of antibiotics of fermentation. In the fermentation industry, the antibiotics are produced as by-products of the growth of molds and bacteria. During operations to recover the antibiotics, the microorganisms are filtered off, usually with the addition of an inorganic filter aid, such as diatomaceous earth. This discarded product is termed "mycelium." The mycelium residue is not considered hazardous, but may cause severe handling odor problems if improperly disposed. Hazardous wastes generated during antibiotic recovery include solvents and still bottoms.

The production of organic medicinal ingredients represents the major source of hazardous wastes in the industry. Of the roughly 90,700 t (100,000 tons) of organic medicinals (excluding antibiotics) produced in the United States in 1973, only about 34,000 t (37,500 tons) were produced by the pharmaceuticals industry itself. The remainder was produced by suppliers closely allied to the industry. Production of organic medicinals resulted in wastes consisting of filter cakes, carbon, filter paper, sewage process sludge, unrecoverable halogenated and nonhalogenated solvents, and still bottoms (6).

TABLE 3. HAZARDOUS WASTES GENERATED BY THE PHARMACEUTICAL INDUSTRY (6)

	1977			
	Nonhazardous		Hazardous	
Industry Segment	Dry Basis	Wet Basis*	Dry Basis	Wet Basis*
Medicinals from animal glands (8,000 t glands/yr)				
Extracted animal tissue	8,400	8,400	--	--
Fats or oils	400	400	--	--
Filter cake (containing protein)	280	560	--	--
Aqueous solvent concentrate	--	--	900	1,800
Total medicinals from animal glands	9,080	9,360	900	1,800
Total for production of active ingredients (SIC Code 2833)	193,000	1,285,000	67,000	70,000
SIC Code 2831: Biological Products				
Aqueous ethanol waste from blood fractionation	--	--	280	680
Antiviral vaccine	--	--	350	350
Other biologicals	--	--	225	225
Total for biological products	--	--	855	1,255
SIC Code 2834: Pharmaceutical Preparations				
Returned goods	11,300	11,300	--	--
Contaminated or decomposed active ingredient	--	--	600	600
Totals for all industry segments:	204,300	1,836,300	70,445	73,755
Rounded to:	204,000	1,836,000	70,000	74,000

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*Wet weight estimates are given for all wastes in metric tons. The two wastes that typically have the highest moisture content are biological sludge and mycelium from fermentations. Where the wet waste estimates are the same as on the dray basis, the waste is usually disposed of with only a minor amount of moisture. However, disposal practices vary from plant to plant, depending on the form in which the waste is produced.

TABLE 4. SUMMARY OF TYPICAL TYPES OF ORGANIC PHARMACEUTICAL HAZARDOUS WASTE MATERIALS (6)

Antibiotics (Penicillin, Tetracyclines, Cephalosporins)

- Recovery Solvents
  - Amyl acetate
  - Butanol
  - Butyl acetate
  - Methylisobutyl ketone
- Purification Solvents
  - Butanol
  - Acetone
  - Ethylene Glycol Monomethyl Ether

Alkaloids (Quinine, Reserpine, Vincristine)

- Extraction Solvents
  - Methanol
  - Acetone
  - Ethanol
  - Chloroform
  - Heptane
  - Ethylene Dichloride
- Purification Solvents
  - Ethylene Dichloride
  - Naphtha
  - Methylene Chloride
  - Benzene

Crude Steroids

- Still bottoms (Soybean Oil Residue)

Medicinals from Animal Organs (Insulin, Heparin)

- Ethanol
- Methanol
- Acetone

Synthetic Organic Medicinals

- Typical Solvents
  - Acetone
  - Toluene
  - Xylene
  - Benzene
  - Isopropyl alcohol
  - Methanol
  - Ethylene Dichloride
  - Acetonitrile
- Organic Residues (Still Bottoms, Sludges, Polymers, Tars)
  - Terpenes
  - Steroids
  - Vitamins
  - Tranquilizers

Blood Plasma Fractions

- Solvent
  - Ethanol

As noted, biodegradability of various waste constituents is the primary factor in determining amenability to biological treatment methods. Struzeski (151, 152), in discussing various nitroanilines used in the production of sulfanilamides, notes that phenol mercury wastes are extremely resistant. Biodegradability testing was cited where the ortho- and meta-nitroaniline were found to be nondegradable. Additional problematic constituents of significance in pharmaceutical wastes are the inorganic constituents, specifically copper, lead, mercury, arsenic, selenium, zinc, chromium, cyanides, and sulfides. The concentrations of some organic and inorganic constituents of drug manufacturing waste are given by Patil et al. (121) and shown in Table 5.

Pulp and Paper Milling

Pulp and paper mills are another source of aqueous hazardous waste streams. Constituents to be expected in such effluents include organic sulfur compounds, phenols, and a variety of oil compounds. Zinc and mercury are also encountered; caustic washing and process stream cooling contribute sodium and aluminum compounds. Quantities of BOD_5 per metric ton of product range between 250 to 500 ppm; total solids are between 350 to 500 kg/t (700 to 1000 kg/ton) of product. In addition, pulp and paper mills can discharge small amounts of cellulose fibers. Such materials are decomposed only by bacteria capable of producing cellulases, enzymes capable of hydrolyzing the cellulose to degradable sugars. Various plant proteins contain sulfur that is converted to hydrogen sulfide during biological degradation. Pulp processing results in the production of excess lignin, a structural polymer. Lignin is a polymer of complex aromatic alcohols and is relatively resistant to biological degradation.

In a survey of 74 bleached kraft mills, the medial mill was found to have a production capacity of 454 t/day (500 tons/day); average flow for such mills is 180 m^3/day (48,000 gals/day). These figures are used in calculating the effluent concentrations shown in Figure 4. In the Development Document for Effluent Limitation Guidelines for the industry (156), the EPA has indicated that the following waste constituents should be controlled:

- BOD_5
- Total suspended Solids (TSS)
- pH
- Color (not including groundwood, deinked and nonintegrated subcategories)
- Ammonia nitrogen (ammonia base sulfite and ammonia base dissolving sulfite only)
- Zinc (groundwood subcategories only)

TABLE 5. DRUG MANUFACTURING WASTES (121)

Parameter	Concn., mg/ℓ
Calcium chloride	600 - 700
Sodium chloride	1,500 - 2,500
Ammonium sulfate	15,000 - 20,000
Calcium sulfate	800 - 21,000
Sodium sulfate	800 - 10,000
Sulfanilic acid, etc.	800 - 1,000
Sulfa drugs	400 - 700
P-Amino phenol, p-Nitrophenolate, p-Nitrochlorobenzene	150 - 200
Amino-nitrozo amino-benzene Antipyrene sulfate	170 - 200
Analogous substances	150 - 200
Var. alcohols	2,500 - 3,000
Benzene, toluene	400 - 700
Chlorinated solvents	600 - 700

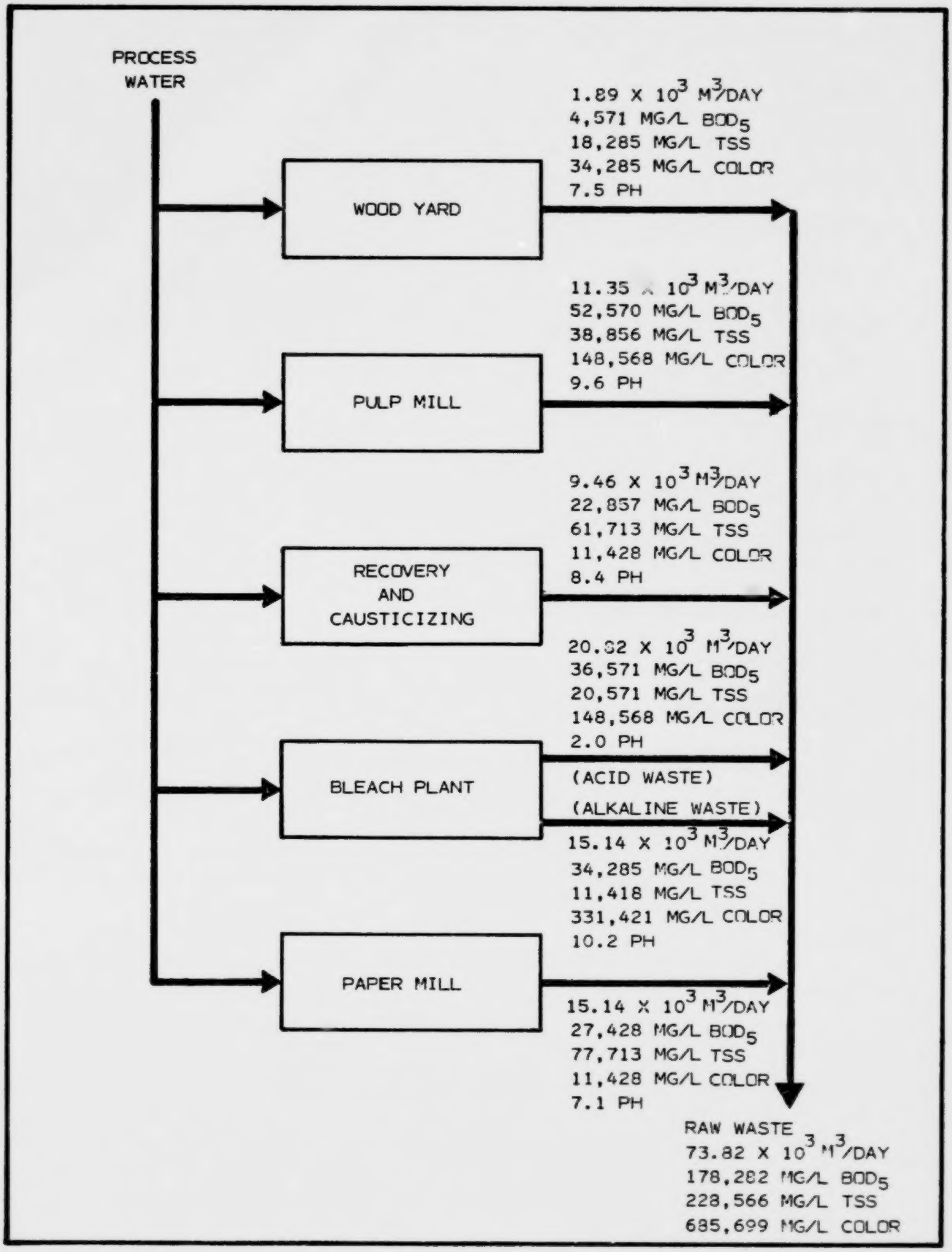
PROCESS WATER
WOOD YARD
1.89 X 10^3 M^3/DAY
4,571 MG/L BOD_5
18,285 MG/L TSS
34,285 MG/L COLOR
7.5 PH
PULP MILL
11.35 X 10^3 M^3/DAY
52,570 MG/L BOD_5
38,856 MG/L TSS
148,568 MG/L COLOR
9.6 PH
RECOVERY AND CAUSTICIZING
9.46 X 10^3 M^3/DAY
22,857 MG/L BOD_5
61,713 MG/L TSS
11,428 MG/L COLOR
8.4 PH
BLEACH PLANT
20.82 X 10^3 M^3/DAY
36,571 MG/L BOD_5
20,571 MG/L TSS
148,568 MG/L COLOR
2.0 PH
(ACID WASTE)
(ALKALINE WASTE)
15.14 X 10^3 M^3/DAY
34,285 MG/L BOD_5
11,418 MG/L TSS
331,421 MG/L COLOR
10.2 PH
PAPER MILL
15.14 X 10^3 M^3/DAY
27,428 MG/L BOD_5
77,713 MG/L TSS
11,428 MG/L COLOR
7.1 PH
RAW WASTE
73.82 X 10^3 M^3/DAY
178,282 MG/L BOD_5
228,566 MG/L TSS
685,699 MG/L COLOR

Figure 4. Effluent characteristics: bleached kraft mill (156).

Other parameters were considered, but were rejected because of their unreliability in the surveyed data or their redundancy in light of other testing.

In addition to the bleached kraft mills, there are other types of pulping mills and paper production mills, including those shown in Table 6.

Steel Making and Coal Gasification

A major industry using coal is the coke production industry. Coke is required in the production of iron ore and other constituents into steel. It is estimated that present U.S. coke production for this industry is approximately 4.93 x 10^7 t/yr (5.4 x 10^7 tons/yr) (11) and will increase in proportion to the increasing steel production.

Gases resulting from the distillation of coal in coke production are subjected to scrubbing and cooling processes to remove contaminants prior to discharge to the atmosphere. In by-product coke ovens, a large portion of the evolved gas is cycled down and used for heating the distillation oven. Process gas used in this manner must be stripped of contaminant hydrocarbons, ammonia, sulfides, and cyanides, or the oven will become plugged and corroded.

The cooling and scrubbing processes are the primary generation points for contaminated aqueous effluents. The most common gas cleaning technology used in the United States is the semi-direct system. Process effluents consist of steam condensate and other wastes from the ammonia still and cooling tower effluents. Excess ammoniacal liquor must also be wasted from the system. These materials may be recovered for process reuse or for the manufacturing of secondary products. However, synthesis of competing products, such as anhydrous ammonia, has limited the cost effectiveness of recovery and placed an increased demand upon process effluent treatment facilities. Table 7 shows a typical analysis of ammoniacal liquor and still waste.

Research of coke oven liquors subjected to treatment by activated sludge processes was conducted for the British Coke Research Association (91). A variety of liquors was described, including limed and unlimed spent liquors and strong, medium, and weak wastes. Data were presented showing the biologically inhibiting constituents such as phenols, thiocyanate, sulfide, chloride, and unknown compounds described in terms of an equivalent permanganate value (Table 8)

The use of coal as an alternative energy source to petroleum will increase substantially in the United States during the remainder of this century. The primary coal conversion processes

TABLE 6. 1972 PRODUCTION BY PULP TYPE AND PAPER GRADES (156)

Pulp[*]	1,000 t (tons)
Special alpha & dissolving	1,521 (1,677)
Sulfite	1,931 (2,130)
Bleached kraft	12,672 (13,970)
Soda	127 (140)
Groundwood	4,188 (4,616)
Paper[†]	
Newsprint	2,360 (2,600)
Tissue	3,106 (3,424)
Fine papers	9,087 (10,017)[#]
Coarse papers	10,310 (11,365)

[*] U.S. Bureau of the Census data.

[†] Grouping of American Paper Institute data.

[#] Includes papers of textile fibers not subject to pulp and paper guidelines.

TABLE 7. TYPICAL ANALYSIS OF AMMONIACAL LIQUOR AND STILL WASTE (44)

	Excess* ammoniacal liquor		Undephenolized still waste		Dephenolized still waste	
	Conc. (ppm)	Discharge kg/10^2 t coke	Conc. (ppm)	Discharge kg/10^3 t coke	Conc. (ppm)	Discharge kg/10^3 t coke
Ammonia	3800	636.4	155	38.6	110	25.0
Phenol	1500	272.7	1320	363.6	158	35.5
Cyanide	20	3.6	--	--	--	--
Thiocyanide	600	90.9	--	--	--	--
Sulfide	2	0.45	--	--	--	--
Chloride	7000	1136.4	4350	1119.1	5400	1468.2
Volume (ℓ/t)	137.7		229.5		187.8	

*Based on analysis of Armco Sttel Corporation, Houston Coke Plant.

TABLE 8. ANALYSES OF COKE OVEN LIQUORS BY THE BRITISH COKE RESEARCH ASSOCIATION (7)

Liquor	Percent of liquor in influent	Loading (kg/1000 m^3 per day)	Influent analyses (mg/ℓ)				
			Phenols	CNS^-	$S_2O_3^{2-}$	Cl^-	Per-manganate value
A not limed	100	2005.0	964	448	308	3532	2680
B not limed	100	1683.8	910	160	158	450	2260
B (synthetic)	100	2711.0	910	160	158	450	2260
C not limed	100	1941.5	840	400	175	6410	2600
D not limed	100	833.1	592	310	168	888	1040
E not limed	50	1923.8	735	690	131	2945	2400
F not limed	100	1843.0	2231	580	728	2041	5000
F not limed	50	3018.2	1116	290	364	1020	2500
G1 not limed	100	1828.5	2335	140	530	2135	4880
G2 not limed	50	2824.0	1400	126	280	968	2340
G2 not limed	40	2245.1	1120	101	224	774	1872
H limed	100	1090.8	530	110	105	2980	1460
I limed	100	1747.4	910	219	247	4690	2555
(H+I)1 limed	100	2199.2	592	97-5	28	1997	1335
(H+I)2 limed	50	1846.2	296	48-8	14	999	668
J limed	60	1076.7	345	441	370	3089	1350
K not limed	100	900.2	Nil	370	120	49	446

planned for commercial scale implementation include gasification, liquefaction, and the production of solvent-refined coal. It is estimated that by 1990, approximately 1.42 x 10^8 m^3/day of synthetic natural gas (SNG) will be produced from coal by approximately 20 standard-size SNG plants each producing 7.1 x 10^6 m^3/day (84). If the United States moves to satisfy 20 percent of the current U.S. oil consumption with coal derived synthetic fuels, then approximately 90 of these plants will be required.

Jahnig and Bertrand (75) discuss the environmental effects of coal gasification processes on water and air quality. Figure 5 shows the estimated process flow rates for a 7.1 x 10^6 m^3/day plant. The gas liquor flow is estimated at 14,500 t/day (16,000 tons/day) and includes the unreacted water or steam from gasification and shift reactions, together with ammonia, phenols, sulfur compounds, cyanides, and thiocyanates. Effluent from waste treatment is estimated to be 4,934 t/day (5,439 tons/day), or 98,682 t/day (109,114 tons/day), if 20 such plants were to be constructed in the United States.

The condensate formed by cooling the raw gas contains water from unreacted steam, together with oil, tar and contaminants from coal decomposition. More of the latter are present in gasification operations at relatively low temperature (926°C or lower). The types of compounds present in this condensate or sour water include sulfur compounds (sulfides, thiophene, etc.), oxygen compounds (phenols, fatty acids, etc.), and nitrogen compounds. Some 60 to 70 percent of the nitrogen in the coal feed is ammonia; other nitrogen compounds are cyanides, amines, pyridine, etc. Thiocyanates, ammonium polysulfides, etc. are a result of the interaction of all these compounds. In general, the amounts of contaminants are comparable to those in the water layer from coal coking operations. In addition, sour water from gasification may have a high content of fatty acids (75).

Textile Processing

Organic compounds commonly used by the textile industry include dyes, surfactants, solvents, finishes, and synthetic fibrous materials. Solvents are used as dye carriers while the surfactants maintain the dye in a dispersed condition, maximizing the fabric coloring processes. Synthetic or cotton and wool fibers may occur in wash waters or spent dye charges. Textile finishes are organic resins that are used to modify the appearance and texture of the treated materials. Sizing agents such as polyvinyl alcohol (PVA) are also used.

Biodegradability studies of textile chemicals indicate that most materials are only marginally amenable to conventional biological treatment and degrade slowly (126). Most dyes show little change during 5-day BOD tests, and there is little color change after 30 days. Nevertheless, inert dyes may be removed by

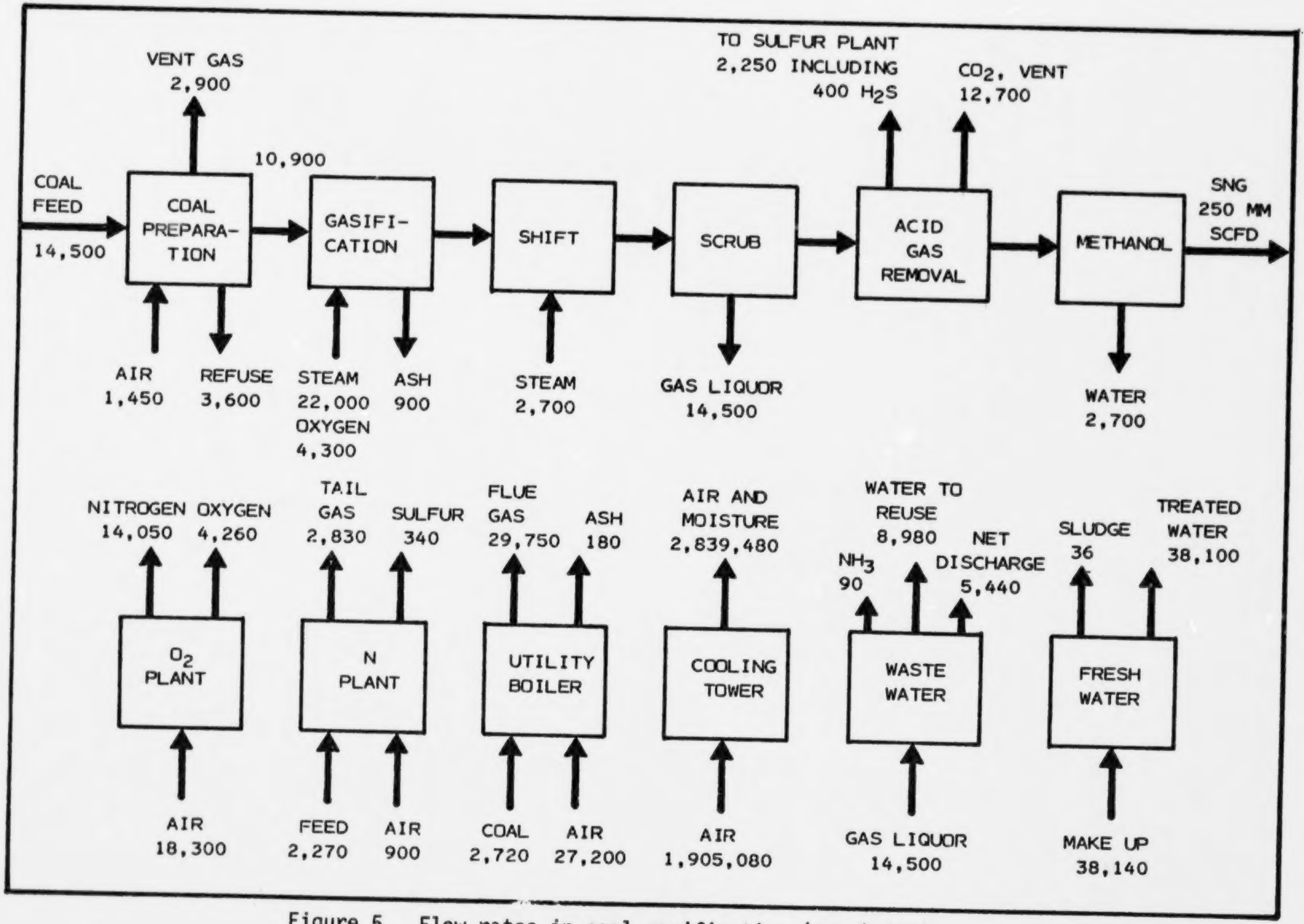
COAL FEED
14,500
COAL PREPARA-TION
VENT GAS
2,900
AIR
1,450
REFUSE
3,600
10,900
GASIFI-CATION
STEAM
22,000
OXYGEN
4,300
ASH
900
SHIFT
STEAM
2,700
SCRUB
GAS LIQUOR
14,500
TO SULFUR PLANT
2,250 INCLUDING
400 H_2S
CO_2, VENT
12,700
ACID GAS REMOVAL
METHANOL
WATER
2,700
SNG
250 MM
SCFD
O_2 PLANT
NITROGEN
14,050
OXYGEN
4,260
AIR
18,300
N PLANT
TAIL GAS
2,830
SULFUR
340
FEED
2,270
AIR
900
UTILITY BOILER
FLUE GAS
29,750
ASH
180
COAL
2,720
AIR
27,200
COOLING TOWER
AIR AND MOISTURE
2,839,480
AIR
1,905,080
WASTE WATER
NH_3
90
WATER TO REUSE
8,980
NET DISCHARGE
5,440
GAS LIQUOR
14,500
FRESH WATER
SLUDGE
36
TREATED WATER
38,100
MAKE UP
38,140

Figure 5. Flow rates in coal gasification (t/yr) (75).

biological systems if the mixed liquor suspended solids are maintained sufficiently high. Under such conditions, dyes have been observed to adsorb onto the biological solids and are removed by subsequent clarification.

Aromatic solvents used by the textile industry can be extremely problematic for biological treatment. Phenolic compounds are especially toxic, and odor problems at plants attempting to treat these compounds have been reported.

The biodegradation of textile dispersants, sizing agents, and finishes depends upon the chemical compounds present in the materials. Polyvinyl alcohol was found to be resistant to biological treatment when it contained acetate groups in the polymer. The efficient hydrolysis of polyvinyl acetate yielding water-soluble alcohol may result in a more readily degradable product. However, the reduction of the polymer acetates may also make stored products less resistant to decay (126). Some dispersants are readily biodegradable, which may be attributable to the emulsive properties. Finishing agents were found to have extremely low BOD values compared to COD. This is attributed to the toxins and metal catalysts used in the formulation of these petrochemical products. Analyses of biological application for treatment of textile wastes have been published and include detailed characterizations of process waste streams. Waste streams in a carpet-yard, fiber-dyeing facility in Rhode Island were analyzed (134), and raw waste parameters and components were characterized (Table 9). In this report, a relationship of COD to TOD (total oxygen demand) concentrations was established where COD equalled 0.98 TOD, 2.51 BOD_5, and 2.54 TOC. However, these ratios are only averages, and there is considerable fluctuation in the sample data.

Evaluation of another full-scale textile plant in Rhode Island (123) indicated that the presence of inorganic salts in waste streams may result in corrosion and adversely impact receiving waters. Dispersants and dye colors may also present operational and discharge problems due to excessive foaming. Heat in process wastes reduces oxygen solubility and adversely impacts sensitive microbial populations in the receiving treatment plant. Composite samples were collected. The variation in the composition of plant discharges with time is shown in Figure 6. The negative impact of such variations upon biological treatment plants can be reduced with the use of surge tanks or equalization lagoons.

GENERAL WASTE QUALITIES

Many of the specific waste constituents and their associated industrial process sources have been described. It may be generally stated that wastewaters from the organic chemical industries exhibit the following characteristics (107):

TABLE 9. A RHODE ISLAND DYEHOUSE RAW WASTE PROFILE AND DYEING CYCLE COMPONENTS (134)

	Avg.	Range
Color - units (tinctorial strength)	2.5	0.7 - 5.9
pH	4.3	4.0 - 6.0
Temperature-^{o}C	43.3	32.2 - 51.1
BOD$_5$ (biochemical oxygen demand) mg/ℓ	396	95 - 700
COD (chemical oxygen demand) mg/ℓ	700	305 - 1450
Suspended Solids - mg/ℓ	27	6 - 70

Calcozine Acrylic Blue HP Cove
Calcozine Acrylic Red B
Dyes* Calcozine Acrylic Violet 3R
Calcozine Acrylic Yellow 3RN
Astrazon Yellow 7GLL

Acetic Acid, 56%
Merpol DA
Retarder 98

Alizarine Light Blue 3F
Dyes Xylene Mill Green B
Melpol DA
Salt
Acetic Acid, 56%
Month Snub
Sulfuric Acid
Erioclarite B
Leveling Agent PD

Dye Omega Chrome Black ALA

Acetic Acid, 56%
Moth Snub

Lanafast Orange RDL
Dyes Lanafast Navy NLF
Lanamid Red 2GL

Acetic Acid, 56%
Emkalana WSDC
Moth Snub

Astrazon Yellow 7GLL
Dyes Astrazon Red GTL
Astrazon Blue 5GL
Acetic Acid, 56%
Merpol DA
Retarder 98
Salt

Sevron Yellow 3RL
Dyes Astrazon Red GTL
Astrazon Blue 5GL
Nabor Blue 2G

Acetic Acid
Merpol DA
Salt

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*Components which develop color of the wastewater are designed above as "Dyes". The other components are used for stabilization, leveling, pH control, etc.

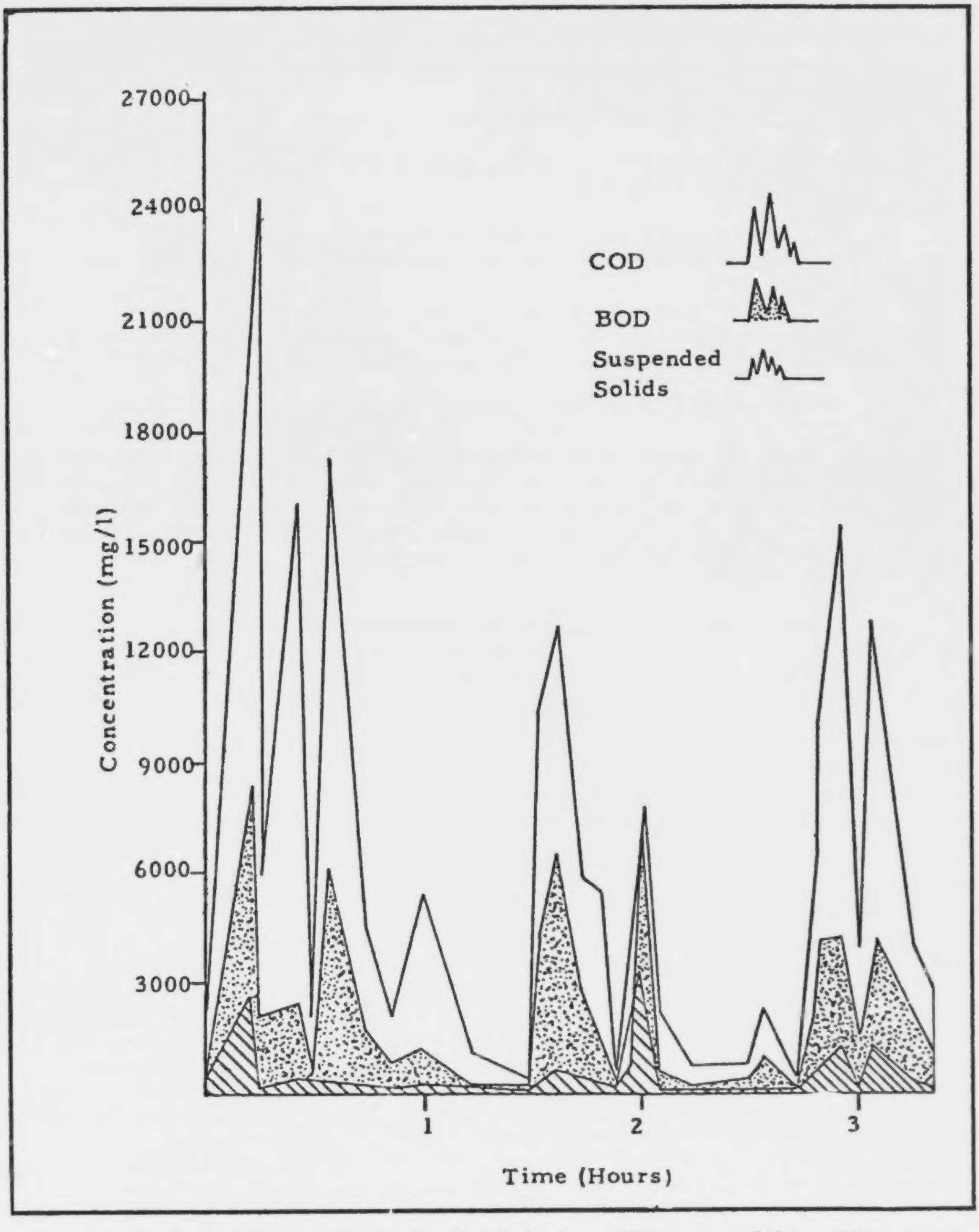

Figure 6. A Rhode Island textile industry effluent profile: COD, BOD, and suspended solids versus time (123).

- High concentrations of COD, consisting of an array of organic compounds with widely varying biological degradability and adsorption characteristics.
- High total dissolved solids
- Small quantities of compounds inhibitory to biological treatment
- Radical variations in waste characteristics as product mix and production processes are altered
- Spills or emergency conditions that can stress or destroy a biological treatment system's microbial population through toxicity or corrosion
- Heavy metals from the catalysts used.

The high level of materials exerting a chemical oxygen demand is attributable in part to acid or caustic wash and steam condensates. Industrial cooling water may be contaminated by system leakage or poor in-plant maintenance. It is common practice to mix cooling water with concentrated organic by-products for dilution prior to discharge.

Washing, scrubbing and crude petroleum desalting all contribute dissolved solids to waste flows. Sodium hydroxide solutions are frequently used in petrochemical processes and can carry sulfur and phenolic compounds, and organic acids. Desalting of crude oils is an important operation in the refining industry and can result in significant discharges of saline water. The high salinity of such process effluents can have a significant impact upon the types of biota that will be present in waste treatment processes. The presence of heavy metals and ammonia nitrogen can also substantially affect the treatment of industrial wastes. The maximum tolerable concentrations of toxic materials in biological waste treatment plants have been reported for many materials. Occasionally, treatability studies have to be made to determine the maximum allowable concentration of the toxic substance in a biological treatment system. In general, the threshold toxicity levels for biological treatment systems are higher than the allowable standards for surface waters. Establishing maximum concentrations for toxins in biological treatment plants is useful only if the quantities of toxins are reduced during the treatment, as is the case with phenols. Often, it is necessary to decrease the concentration of the toxic material by pretreatment. However, it is necessary to guard against the so-called synergistic effect of certain materials. One industry may be allowed to discharge zinc below the toxic level, another industry may be allowed to do the same with copper. The resulting combination of both discharges will have a synergistic effect and may cause biological deterioration in the receiving stream or the treatment plant.

Ammonia nitrogen is present in many natural waters in relatively low concentrations, while industrial streams often contain exceedingly high concentrations of ammonia. Nitrogen in excess of 1,600 mg/ℓ has proven to be inhibitory to many microorganisms present in the activated sludge basin. Sulfides are present in many wastewaters either as a mixture of $HS-H_2S$ (depending on pH), sulfonated organic compounds, or metallic sulfides.

The influence of heavy metals on biological processes has been the subject of many investigations. Toxic thresholds for copper, zinc and cadmium have been established at approximately 1 mg/ℓ.

There is a potential for the continuous introduction of organic toxins and heavy metals in a manner that will significantly affect the quality of the microbial populations in treatment plants. Such materials may be trace constituents which may play important roles in determining the in-plant kinetics of bioconversion. There is always opportunity for accidental spills or process breakdown which can result in the discharge of concentrated "slugs" of marginally degradable organics or toxic materials to the treatment system. When these types of waste fluctuations occur, they can affect the treatment system in the following ways:

- Reduction in the BOD and COD removal efficiencies
- Alteration of solids settling characteristics in the primary or secondary clarifiers (increased solids in plant effluents)
- Accumulation of odor generating compounds in quiescent tanks or lagoons
- Clogging of biological trickling filters.

The seriousness of these conditions depends upon the extent to which the microbial population has been altered and the quantity of solids and toxic compounds that has accumulated in the system. Very mild system upsets have been observed where new types of organic compounds are introduced. In certain cases, after an initial lag period, the microbial population will acclimate to the new waste and begin assimilating the material. In contrast, the introduction of concentrated wastes containing high levels of toxins or corrosives may result in the system "souring". Inorganic compounds present in organic chemical industry wastewaters include a number of metal and nonmetal compounds. Trace metals may interfere with the metabolic biochemistry of microorganisms. Caustics and nonmetals can destroy cellular membranes and microbial tissues.

Chemical industrial wastes pose additional problems to receiving treatment plants or environments. In petroleum refining and pulp and petrochemical processing, some aqueous process streams have been in direct or indirect contact with exothermal reactions or heated vessels. The elevated temperature of these effluents has a demonstrated impact upon the ecological composition of the receiving environment. Waste temperatures in excess of 40°C will tend to favor thermophilic microbial species. Populations of these types of bacteria are not as resistant to process fluctuations and may also inhibit the settling of biological flocs during secondary clarification. Nevertheless, mild increases in waste temperatures may actually enhance biological metabolism in colder climates; the optimum temperature is usually between 30 and 37°C.

Another important characteristic of organic industrial waste streams is the relative imbalance of nutrient compounds. Petroleum contaminants in such streams are products of raw feedstocks comprised chiefly of carbon compounds. The high concentrations of these carbonaceous wastes in relation to any nitrogenous or phosphorous compounds make them difficult to biologically degrade in the receiving environment. It is generally stated that the optimum carbon:nitrogen:phosphorus ratio is 100:10:1. Studies of the microbial aspects of petroleum degradation agree that nitrogen and phosphorus are the limiting elements in environmental biodegradation of materials such as crude oil.

Significant enhancement of biological growth on oil (from 3 to 70 percent) with additions of nitrate and phosphate have been reported (31). Nutrient addition may be accomplished by the addition of chemicals such as ammonia and phosphoric acid or by mixing nutrient-deficient wastes with nutrient-rich waste streams. Ammonia-rich wastes, such as those from fertilizer manufacturing plants, can be treated biologically (71) and may be mixed with carbonaceous wastes. Ammonia may also be present in condensates from refining or coking processes, and nitric acid is often present in wastes discharged from aromatic nitration processing (50). Phosphates and polyphosphates appearing in cooling and boiler waters (where they are used for corrosion control) can provide a phosphorus input to biological treatment. Phosphoric acid is also used as a catalyst in polymerization, alkylation, and isomerization processes and may appear in aqueous waste streams from those processes (50).

In some industrial waste streams, certain nutrient compounds may be present in excess. When such effluents are discharged into lakes, ponds, and surface streams, the presence of nitrogen and phosphorus is particularly undesirable, since it can enhance eutrophication of the receiving waters. The chemical form in which nutrients are present may differ and vary with the degree of treatment. Nitrogen can be present as ammonia, nitrate, nitrite, and organic nitrogen in the form of proteins, urea, and amino acids. Phosphorus can be present as orthophosphates or organic phosphorus (8).

Nutrient assimilation and removal by biological treatment processes is, therefore, an important factor in ensuring efficient industrial waste treatment as well as protection of receiving waters. Insoluble organic materials are present in most industrial effluents, and concentrations of organic solvents, greases, or oils that are immiscible in water will tend to partition in treatment process units. Synthetic textile fibers, paper, cotton, and resin column beads are also in this category.

The partitioning characteristics of organic liquids are usually used to effect separation and treatment. Lighter-than-water materials that are not removed by in-plant processes or pretreatment can be treated at the receiving plant by using skimmers (98) or API-type oil/water separators. If highly volatile materials such as gasoline and ether are present, they may be toxic and can generate odorous and explosive vapors. Excessive quantities of such materials must be removed prior to discharge to the biological treatment plant. Heavier-than-water materials and other organic solids will usually be removed by primary sedimentation units. Such materials are reported to be low in nitrogen and phosphorus content, and nutrient deficiency can result if primary removal is inefficient and loading to the bioreactor is too high (98).

CLASSES OF ORGANIC WASTES NOT AMENABLE TO BIODEGRADATION

Most organic compounds are, to a greater or lesser extent, biodegradable. Yet a variety of materials, because of their toxic, complex, or inert nature, cannot be degraded by treatment plant microbes during the conventional retention period. A number of innovative operational and plant design approaches have been suggested to enhance the biological degradation of these organics. These are the main topic of this report.

Nevertheless, there remain certain classes of compounds that are extremely refractory and cannot be biologically treated. The impact of such materials upon the treatment system is, of course, dependent upon the concentration introduced and the contact period with and species present in the microbial population. System poisoning may be avoided by storing extremely toxic or concentrated wastes in spill tanks or lagoons. The waste may then be mixed with other influents at a low rate to ensure adequate dilution in the bioreactor. However, such an approach may not be economically feasible if the production volume of such wastes is large and continuous.

The petrochemical industry is plagued by a number of compounds which, when present in waste streams in concentrations above certain limits, are a problem to biological treatment. A list of identified problem concentrations for a number of materials is shown in Table 10. Much information about the relative degradability of compounds has been derived through laboratory manometric and batch culture studies (67).

TABLE 10. PROBLEM CONCENTRATIONS OF TESTED MATERIALS AS DETERMINED BY MANOMETRIC INVESTIGATIONS (67)

	Problem Concentration (mg/ℓ)	
Chemical	Substrate Limiting	Non-Substrate Limiting
n-Butanol	--	>1000
sec-Butanol	--	>1000
t-Butanol	>1000	>1000
Allyl alcohol	--	>1000
2-Ethyl-1-hexanol	500-1000	--
Formaldehyde	--	50-100
Crotonaldehyde	∼200	50-100
Acrolein	--	20-50
Acetone	--	>1000
Methyl isobutyl ketone	>1000	100-300
Isophorone	>1000	--
Diethylamine	--	300-1000
Ethylene diamine	--	100-300
Acrylonitrile	150-500	100
2-Methyl-5-ethylpyridine	>1000	100
N,N-dimethylaniline	>1000	--
phenol	>1000	300-1000
Ethyl benzene	>1000	--
Sodium benzoate	--	>300
Ethylene dichloride	150-500	--
Ethyl acrylate	600-1000	300-600
Sodium acrylate	--	>500
Dodecane	>1000	--
Dextrose	>1000	>1000
Ethyl acetate	>1000	--
Ethylene glycol	>1000	>900
Diethylene glycol	--	>1000
Tetralin	>1000	--
Kerosene	--	>500
Cobalt chloride	--	>1000

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*Compound was arbitrarily classified as a problem when the activity ratio was less than 0.5. The 0.5 level was considered to be a decrease of more than 50 percent of the total gas production over that in the unfed manometric control.

Different organic compounds at the same concentration will have varying impacts upon microbes with resultant levels of biodegradability depending upon environmental and chemical conditions. Numerous studies of the degradation of hydrocarbons in marine and fresh-water environments indicate that diauxic growth may be an important governing factor in determining degradation of mixed food substrates (77). It is apparent that some, but not all, organisms have a preference for peptones, carbohydrates, and other forms of readily usable carbon sources over hydrocarbons or synthetic organic compounds (77). The sequential utilization of preferred substrates from a mixture has also been demonstrated for various classes of hydrocarbon and synthetic organic molecules. Investigators (77) have noted the preference that bacterial mixed cultures have for n-alkane molecules of light molecular weight. The following generalizations may be drawn concerning diauxic growth in mixed industrial wastes:

- Non-aromatic or cyclic aromatic compounds are preferred over aromatics.

- Materials with unsaturated bonds in their molecules, e.g., alkenes, alkynes, tertiary amines, etc., are preferred over materials exhibiting saturated bonding.

- The comparative stereochemistry of the molecules of certain compounds makes them more or less susceptible to attack by microbial enzymes. The n-isomers of the lighter weight molecules are preferred over branched isomers and complex, polymeric substances.

- Soluble organic compounds are usually more readily degraded than insoluble materials. Biological waste treatment is most efficient in removing dissolved or colloidal materials whichare more readily attached by enzymes and transported through cell membranes. Readily dispersed compounds are usually degraded more rapidly because of the increased surface area that is presented to the individual microorganisms.

- The presence of key functional groups at certain locations in the molecules can make a compound more or less amenable to biodegradation. Alcohols, for example, are often more readily degraded than their alkane or alkene homologues. On the other hand, halogenation of certain hydrocarbons may make them resistant to degradation.

Reports of research on aerobic biological oxidation have identified the following classes of wastes as generally resistant:

- Oil
- Isoprene
- Methyl vinyl ketone
- Morpholine
- Ethers
- Ethylene chlorohydrin
- Polymeric compounds
- Polypropylene benzene sulfonates
- Tertiary and volatile aliphatics
- Aromatics
- Alkyl-aryl groups
- Tertiary aliphatic alcohols
- Tertiary benzene sulfonates
- Trichlorophenols

Biodegradability in complex waste mixtures is not identical to that in laboratory experiments. Some organic materials can polymerize or react in a synergistic manner upon contact with other wastes. Acclimation of microorganisms can also affect biodegradability. The lack of sufficient acclimation of a biological seed to the waste sample has probably been the major source of contradictory data and misunderstanding of treatability studies (50). Recent treatability studies have taken these problems into account in attempting to utilize realistic activated sludge specimens to degrade complex organic substrates.

Pitter (122) used activated sludge inocula adapted to various test substrates to compare the biological degradability of a number of organic compounds. Results of these experiments are shown in Tables 11 through 13. The experiments were conducted until there was no detectable decrease in COD. The total percentage of COD removed and rate of degradation were evaluated. Materials were considered readily biodegradable if 90 percent or more of the initial COD was removed in 120 hr of incubation. Only a low or zero removal of COD was achieved with refractory compounds such as pyrogallol, metol and nitroanilines.

Other treatability studies have determined the ratio of BOD_5 and COD of wastewater compounds (46). This ratio indicates the fraction of dichromate-oxidizable materials which is amenable to biological degradation. A high ratio, for example, would indicate that many of the dissolved organic materials can be degraded biologically, while a low value would indicate the presence of a significant fraction of bioresistant organic constituents. Table 14 shows the measured BOD and COD as a percent of theoretical oxygen demand for several classes of chemicals. Note the relatively high degradability of most unsubstituted aliphatic compounds.

REQUIRED DEGREE OF TREATMENT

Amendments to Public Law 92-500 control the discharges of hazardous industrial waste effluents. Foremost among these is the National Pollutant Discharge Elimination System (NPDES), 33 U.S.C. 1251 (incorporated as Section 402), which establishes effluent discharge limitations of waste constituents. Permits issued in

TABLE 11. BIOLOGICAL DEGRADABILITY OF AROMATIC COMPOUNDS (122)

Compound	Percent Removed (based upon COD)	Rate of biodegradation (mg COD g^{-1} h^{-1})
Aniline	94.5	19.0
Aminophenolsulphonic acid	64.6	7.1
Acetanilide	94.5	14.7
p-Aminoacetanilide	93.0	11.3
o-Aminotoluene	97.7	15.1
m-Aminotoluene	97.7	30.0
p-Aminotoluene	97.7	20.0
o-Aminobenzoic acid	97.5	27.1
m-Aminobenzoic acid	97.5	7.0
p-Aminobenzoic acid	96.2	12.5
o-Aminophenol	95.0	21.1
m-Aminophenol	90.5	10.6
p-Aminophenol	87.0	16.7
Benzenesulphonic acid	98.5	10.6
m-Benzenedisulphonic acid	63.5	3.4
Benzaldehyde	99.0	119.0
Benzoic acid	99.0	88.5
o-Cresol	95.0	54.0
m-Cresol	95.5	55.0
p-Cresol	96.0	55.0
D-Chloramphenicol	86.2	3.3
o-Chlorophenol	95.6	25.0
p-Chlorophenol	96.0	11.0
o-Chloroaniline	98.0	16.7
m-Chloroaniline	97.2	6.2
p-Chloroaniline	96.5	5.7
2-Chloro-4-nitrophenol	71.5	5.3
2,4-Dichlorophenol	98.0	10.5
1,3-Dinitrobenzene	0	--
1,4-Dinitrobenzene	0	--
2,3-Dimethylphenol	95.5	35.0
2,4-Dimethylphenol	94.5	28.2
3,4-Dimethylphenol	97.5	13.4
3,5-Dimethylphenol	89.3	11.1
2,5-Dimethylphenol	94.5	10.6
2,6-Dimethylphenol	94.3	9.0
3,4-Dimethylaniline	76.0	30.0
2,3-Dimethylaniline	96.5	12.7
2,5-Dimethylaniline	96.5	3.6
2,4-Diaminophenol	83.0	12.0
2,5-Dinitrophenol	see note 1	
2,6-Dinitrophenol	see note 1	
2,4-Dinitrophenol	85.0	6.0
3,5-Dinitrobenzoic acid	50.0	--
3,5-Dinitrosalicylic acid	0	--
Furfuryl alcohol	97.3	41.0

TABLE 11 (continued)

Compound	Percent Removed (based upon COD)	Rate of Biodegradation (mg COD g^{-1} h^{-1})
Furfurylaldehyde	96.3	37.0
Gallic acid	90.5	20.0
Gentisic acid	97.6	80.0
p-Hydroxybenzoic acid	98.7	100.0
Hydroquinone	90.0	54.2
Isophthalic acid	95.0	76.0
Metol	59.4	0.8
Naphtoic acid	90.2	15.5
1-Naphthol	92.1	38.4
1-Naphthylamine	0	0
1-Naphthalenesulfonic acid	90.5	18.0
1-Naphthol-2-sulphonic acid	91.0	18.0
1-Naphthylamine-6-sulphonic acid	0	0
2-Naphthol	89.0	39.2
p-Nitroacetophenone	98.8	5.2
Nitrobenzene	98.0	14.0
o-Nitrophenol	97.0	14.0
m-Nitrophenol	95.0	17.5
p-Nitrophenol	95.0	17.5
o-Nitroluene	98.0	32.5
m-Nitrotoluene	98.5	21.0
p-Nitrotoluene	98.0	32.5
o-Nitrobenzaldehyde	97.0	13.8
m-Nitrobenzaldehyde	94.0	10.0
p-Nitrobenzaldehyde	97.0	13.8
o-Nitrobenzoic acid	93.4	20.0
m-Nitrobenzoic acid	93.4	7.0
p-Nitrobenzoic acid	92.0	19.7
o-Nitroaniline (see note 2)	0	--
m-Nitroaniline (see note 2)	0	--
p-Nitroaniline (see note 2)	0	--
Phthalimide	96.2	20.8
Phthalic acid	96.8	78.4
Phenol	98.5	80.0
Phloroglucinol	92.5	22.1
N-Phenylanthranilic acid	28.0	--
o-Phenylendiamine (see note 3)	33.0	--
m-Phenylendiamine (see note 3)	60.0	--
p-Phenylendiamine (see note 3)	80.0	--
Pyrocatechol	96.0	55.5
Pyrogallol	40.0	--
Resorcinol	90.0	57.5
Salicylic acid	98.8	95.0
Sulphosalicylic acid	98.5	11.3
Sulphanilic acid	95.0	4.0

TABLE 11 (continued)

Compound	Percent Removed (based upon COD)	Rate of Biodegradation (mg COD g^{-1} h^{-1})
Thymol	94.6	15.6
p-Toluenesulphonic acid	98.7	8.4
2,4,6-Trinitrophenol	0	--

Note 1. 2,5 and 2,6-dinitrophenol were at higher concentrations not degraded. 2,6-Dinitrophenol was at lower concentrations decomposed with long adapted activated sludge (40 days). 2,5-Dinitrophenol was biochemically stable.

Note 2. The degradation of nitroanilines was determined photometrically in the concentration range from 25 to 30 mg l^{-1}.

Note 3. The degradation of phenylenediamines was determined photometrically in the concentration range from 25 to 30 mg l^{-1}. p-Phenylenediamine was comparatively well degradable.

TABLE 12. BIOLOGICAL DEGRADABILITY OF CYCLOALIPHATIC COMPOUNDS (122)

Compound	Percent Removed (based upon COD)	Rate of Biodegradation (mg COD g^{-1} h^{-1})
Borneol	90.3	8.9
Caprolactam	94.3	16.0
Cyclohexanol	96.0	28.0
Cyclopentanol	97.0	55.0
Cyclohexanone	96.0	30.0
Cyclopentanone	95.4	57.0
Cyclohexanolone	92.4	51.5
1,2-Cyclohexanediol	95.0	66.0
Dimethylcyclohexanol	92.3	21.6
4-Methylcyclohexanol	94.0	40.0
4-Methyleyclohexanone	96.7	62.5
Menthol	95.1	17.7
Tetrahydrofurfuryl alcohol	96.1	40.0
Tetrahydrophthalimide	0	--
Tetrahydrophthalic acid	0	--

TABLE 13. BIOLOGICAL DEGRADABILITY OF ALIPHATIC COMPOUNDS

Compound	Percent Removed (based upon COD)	Rate of Biodegradation (mg COD g^{-1} h^{-1})
Ammonium oxalate	92.5	9.3
n-butanol	98.8	84.0
Sec. butanol	98.5	55.0
Tert. butanol	98.5	30.0
1,4-Butanediol	98.7	40.0
Diethylene glycol	95.0	13.7
Diethanolamine	97.0	19.5
Ethylene diamine	97.5	9.8
Ethylene glycol	96.8	41.7
Glycerol	98.7	85.0
Glucose	98.5	180.0
n-Propanol	98.8	71.0
Iso-Propanol	99.0	52.0
Triethylene glycol	97.7	27.5

TABLE 14. COMPARISON OF COD, BOD, AND ThOD WITH RESPECT TO THEORETICAL ORGANIC CHEMICALS (46)

Chemical Group	ThOD (mg/mg)	Measured COD (mg/mg)	$\frac{COD}{ThOD}$ (%)	Measured BOD_5 (mg/mg)	$\frac{BOD_5}{ThOD}$ (%)
Aliphatics					
Methanol	1.50	1.05	70	1.12	75
Ethanol	2.08	2.11	100	1.58	76
Ethylene glycol	1.26	1.21	96	0.36	29
Isopropanol	2.39	2.12	89	0.16	7
Maleic acid	0.83	0.80	96	0.64	77
Acetone	2.20	2.07	94	0.81	37
Methylethyl ketone	2.44	2.20	90	1.81	74
Ethyl acetate	1.82	1.54	85	1.24	68
Oxalic acid	0.18	0.18	100	0.16	89
			avg. 91		avg. 56
Aromatics					
Toluene	3.13	1.41	45	0.86	28
Benzaldehyde	2.42	1.98	80	1.62	67
Benzoic acid	1.96	1.95	100	1.45	74
Hydroquinone	1.89	1.83	100	1.00	53
o-Cresol	2.52	2.38	95	1.76	70
			avg. 84		avg. 58
Nitrogenous organics					
Monoethanolamine	2.49	1.27	51	0.83	34
Acrylonitrile	3.17	1.39	44	nil	0
Aniline	3.18	2.34	74	1.42	44
			avg. 58		avg. 26
Refractory					
Tertiary-butanol	2.59	2.18	84	0	0
Diethylene glycol	1.51	1.06	70	0.15	10
Pyridine	3.13	0.05	2	0.06	2
			avg. 52		avg. 4

compliance with NPDES specify the limitations and monitoring requirements that must be implemented in order to comply with the Water Pollution Control Act. In addition, the permits may specify details about responsibility for compliance between treatment and joint industrial facilities that might contribute waste streams to the former. To encourage maximization of pollutant removal, the permits may further specify that industrial waste stream sources provide monitoring of their effluents and report such information to receiving treatment plants. The permit also establishes daily average and daily maximum effluent limitations for each waste stream source. The typical characteristics measured in a petrochemical plant effluent are:

- BOD_5
- COD
- TSS
- Oil and grease
- NH_3-N
- Chromium
- Phenols
- R-C_1
- Phosphorus
- Fluoride
- Cyanide
- Mercury
- Lead
- Arsenic
- TKN
- Flow
- Temperature
- pH

Sections 304, 306 and 307 of the Federal Water Pollution Control Act Amendments of 1972 give the EPA the responsibility for establishing effluent limitations guidelines for industrial discharges.

Organic Chemicals Industry

The EPA contractor conducting the study to fulfill the requirements of the above sections indicated four subcategories of effluent limitations for different groups of organic chemicals industries:

- Nonaqueous processes - Contact between water and reactants or products is minimal. Water is not required as reactant or diluent and is not formed as a reaction product, but is only used for periodic washes or catalyst hydration.

- Process with process water contact as steam diluent or absorbent - Process water is in the form of dilution steam, direct product quench, or absorbent for effluent gases. Reactions are all vapor-phase over solid catalysts. Most processes have an absorber coupled with steam stripping of chemicals for purification and recycle.

- Continuous liquid-phase reaction systems - Reactions are liquid-phase, the catalyst in an aqueous medium. Continuous regeneration of the catalyst requires extensive water usage, and substantial removal of spent inorganic by-products may be required. Additional process water is involved in final purification or neutralization of products.

- Batch and semi-continuous processes - cleaning of noncontinuous production equipment; most reactions are liquid-phase with aqueous systems. Material handling is characteristically manual.

Separate limitations for BOD_5, COD, phenols, and TSS are developed for each of the subcategories.

In establishing effluent limitation guidelines and new source performance standards for the organic chemicals industry (113), the EPA subcontractor reviewed and summarized historic treatment plant data. Based on that information, conclusions were made relative to the reduction of effluent constituents according to three levels of treatment technology:

- Best Practicable Control Technology Currently Available (BPCTCA)

- Best Available Technology Economically Achievable (BATEA)

- Best Available Demonstrated Control Technology (BADCT)

A summary of the treatment plant survey data for exemplary plants is shown in Table 15 (149). The average reduction in COD was 72 percent; average reductions in BOD and TOC were 87 and 58 percent, respectively. To meet BATEA treatment guidelines, the EPA has called for an effluent concentration of 10 mg/ℓ TSS, as well as 69 and 90 percent reductions in BOD and COD, respectively.

For BADCT treatment, the EPA recommends the following level of performance above the BPCTCA level:

Parameter	Percent Reduction Factors Beyond BPCTCA Effluent Limitation	Minimum Monthly Average Effluent Concentration (mg/ℓ)
BOD	17	10
COD	20	-
TSS	0	10

Additional parameters surveyed during the EPA guidelines study included phenols, ammonia nitrogen, cyanide, sulfates, and pH.

Pulp and Paper Milling

Prior to the passage of the 1972 Amendments to the Federal Water Pollution Control Act, to facilitate processing of the Refuse Act discharge permit applications, the EPA had assembled criteria for the pulp industry. These criteria (Effluent limitation Guidance) were distributed on June 9, 1972. The EPA

TABLE 15. TREATMENT PLANT SURVEY DATA[*] (113).

Plant No.	Treatment System	Category	COD % Removal	COD Effluent mg/ℓ	Total BOD % Removal	Total BOD Effluent mg/ℓ	TOC % Removal mg/ℓ	TOC Effluent mg/ℓ	TSS % Removal	TSS Effluent mg/ℓ	TDS Effluent mg/ℓ	Oil & Grease Effluent mg/ℓ
2[**]	AS-AL	C	64	2,300	90	427	32	2,710	Negative	4,700	2,300	--
3[**]	AS	D	71	284	73	74	71	132	Negative	62	3,100	1[†]
4[**]	AS	B	57	214	82	13	35	80	40	14	2,900	4[†]
5[**]	TF-AS	B	59	133	92	12	43	61	97	44	1,430	2[†]
6[**]	AL	B-C	66	980	73	235	11	573	Negative	362	3,000	11[†]
8[**]	AL	B	69	92	84	6	26	52	99	3	690	--
9[**]	AS	C	75	595	92	75	69	242	Negative	50	3,810	12[†]
11[**]	AS-AL	C	94	337	99	16	27	343	Negative	145	2,690	1[†]
13[**]	AS	B-C	65	940	90	177	64	470	120	338	1,520	6[†]
16[**]	AS	D	54.8	1,650	82.1	300	80.8	280	43.6	552	10,990	226[‡]
17[**]	AS	D	60.0 77.3	1,400 1,000	81.4 90.0	240 310	63.4 76.8	410 360	Negative	1,300 732	3,750 4,060	24[‡] 22[‡]
18[**]	AS	D	22.1	2,680	16.7	650	--	1,025	42.9	1,170	2,050	106[‡]
19[**]	AS	D	59.5	5,100	69.8	1,800	55.8	1,700	Negative	2,500	8,360	--
20[**]	AS	C	96.2	317	99.5	19	96.6	114	Negative	100	1,950	19[‡]
21	AL	C	62	600	78	27	66	47	89	30	9,800	--
22	AS	B	16.1	1,370	47.5	210	8.3	550	53.4	82	15,400	<.03[‡]
23	AS	B	95.4	147	92.6	41	95.4	35	Negative	37	580	21[‡]
Average[#]			72		87		58					

[*] Based on 24-hr composite samples.

[**] Plants considered to be exemplary in performance based on historical data.

[†] Oil and grease are reported as carbon tetrachloride extractables.

[‡] Oil and grease are reported as Freon extractables.

[#] Includes exemplary plants as well as Plant 23.

then authorized a study to provide additional information on effluent limitations for the unbleached kraft, semi-chemical and paperboard segments of the industry which was published as proposed effluent limitations in the EPA Development Document in January 1972 (102).

In 1976, the EPA published detailed guidelines for all major subcategories of the pulp and paper industry (156). Subcategories included groundwood, sulfite, bleached kraft, soda, deink and the nonintegrated paper mills segment of the pulp, paper, and paper board point source category. Effluent limitations for BPCTCA for various subcategories as presented in the guidelines as shown in Table 16.

Steel Making and Coal Gasification

The EPA has presented a development document outlining the effluent limitations guidelines and new source performance standards for the steel making segment of the iron and steel manufacturing industry (38). Table 17 shows the derived maximum thirty-day average effluent limitations for eleven subcategory processes including by-product coke and beehive coke operations. Typical products from the by-product type of operation include gas, tar, tar acids, hydrogen sulfide, light oil, coke and coke breeze, In the beehive process, only coke is produced and no other by-products are recovered. Water is used only for coke quenching. The third category which is numerically limited in oil and grease discharge is the continuous casting processes which generate oily waste products from machine cooling and spraying.

Textile Processing

Table 18 shows the maximum thirty-day average effluent limitations guidelines for BPCTCA treatment for various process categories of the textile processing industry (47). Commission finishers are allocated 100 percent of the guidelines for the thirty-day maximum levels. These types of operations process material upon demand according to the customer's specification. Control of production scheduling and process flows is therefore difficult and subject to varying demand.

TABLE 16. BPCTCA EFFLUENT LIMITATIONS IN kg/t (156)*

	Maximum 30-Day Average				Maximum Day			
Subcategory	BOD_5	(mg/ℓ)	TSS	(mg/ℓ)	BOD_5	(mg/ℓ)	TSS	(mg/ℓ)
Dissolving Kraft	12.25	(24.5)	20.05	(40.1)	23.6	(47.2)	37.3	(74.6)
Market Kraft	8.05	(16.1)	16.4	(32.8)	15.45	(30.9)	30.4	(60.8)
BCT Kraft	7.1	(14.2)	12.9	(25.8)	13.65	(27.3)	24.0	(48.0)
Fine Kraft	5.5	(11.0)	11.9	(23.8)	10.6	(21.2)	22.15	(44.3)
Papergrade Sulfite (Blow Pit Wash)								
Bisulfite-Surface	16.55	(33.1)	23.65	(47.3)	31.8	(63.6)	43.95	(87.9)
Bisulfite-Barometric	18.05	(36.1)	28.1	(56.2)	34.7	(69.4)	52.2	(104.4)
Acid Sulfite Surface	16.8	(33.6)	23.65	(47.3)	32.3	(64.6)	43.95	(87.9)
Acid Sulfite-Barometric	18.5	(37.0)	28.1	(56.2)	35.55	(71.1)	52.2	(104.4)
Papergrade Sulfite (Drum Wash)								
Bisulfite-Surface	13.9	(27.8)	23.65	(47.3)	26.7	(53.4)	43.95	(87.9)
Bisulfite-Barometric	15.3	(30.6)	28.1	(56.2)	29.4	(58.8)	52.2	(104.4)
Acid Sulfite-Surface	15.5	(31.0)	23.65	(47.3)	29.75	(59.5)	43.95	(87.9)
Acid Sulfite-Barometric	16.9	(33.8)	28.1	(56.2)	32.5	(65.0)	52.2	(104.4)
Continuous Digesters	19.85	(39.7)	28.95	(57.9)	38.15	(76.3)	53.75	(107.5)
Dissolving Sulfite								
Nitration	21.55	(43.1)	38.05	(76.1)	41.4	(82.8)	70.65	(141.3)
Viscose	23.05	(46.1)	38.05	(76.1)	44.3	(88.6)	70.65	(141.3)
Cellophane	25.0	(50.0)	38.05	(76.1)	48.05	(96.1)	70.65	(141.3)
Acetate	26.45	(52.9)	38.05	(76.1)	50.8	(101.6)	70.65	(141.3)

*Qualified by allowances for barking, chip washing, log flumes or ponds, and noncontinuous discharges.

TABLE 16 (continued)

Subcategory	Maximum 30-Day Average		Maximum Day	
	BOD_5 (mg/ℓ)	TSS (mg/ℓ)	BOD_5 (mg/ℓ)	TSS (mg/ℓ)
GW-Chemi-Mechanical	7.05 (14.1)	10.65 (21.3)	13.5 (27.0)	19.75 (39.5)
GW-Thermo-Mechanical	5.55 (11.1)	8.35 (16.7)	10.6 (21.2)	15.55 (31.1)
GW-CMN Papers	3.9 (7.8)	6.85 (13.7)	7.45 (14.9)	12.75 (25.5)
GW-Fine Papers	3.6 (7.2)	6.3 (12.6)	6.85 (13.7)	11.75 (23.5)
Soda	7.1 (14.2)	13.2 (26.4)	13.7 (27.4)	24.5 (49.0)
Deink	9.4 (18.8)	12.95 (25.9)	18.1 (36.2)	24.05 (48.1)
NI Fine Papers	4.25 (8.5)	5.9 (11.8)	8.2 (16.4)	11.0 (22.0)
NI Tissue Papers	6.25 (12.5)	5.0 (10.0)	11.4 (22.8)	10.25 (20.5)
NI Tissue Papers (FWP)	7.1 (14.2)	9.2 (18.4)	13.7 (27.4)	17.05 (34.1)

pH for all subcategories shall be within the range of 5.0 to 9.0

Subcategory	Zinc**	
	Maximum 30-Day Average	Maximum Day
GW-Chemi-Mechanical	0.17 (0.34)	0.34 (0.68)
GW-Thermo-Mechanical	0.13 (0.26)	0.26 (0.52)
GW-CMN Papers	0.15 (0.30)	0.30 (0.60)
GW-Fine Papers	0.135 (0.27)	0.275 (0.55)

[**] Applicable only to mills using zinc hydrosulfite.

TABLE 17. MAXIMUM THIRTY-DAY AVERAGE EFFLUENT LIMITATIONS GUIDELINES: IRON AND STEEL INDUSTRY (38)

Subcategory	Cyanide	Phenol	Ammonia	Sulfide	Oil & Grease	Suspended Solids	pH
By-product coke	0.0219	0.0015	0.0912	--	0.0109	0.0365	6.0 to 9.0
Beehive coke	No discharge of process wastewater pollutants to navigable waters.						
Sintering	--	--	--	--	0.0021	0.0104	6.0 to 9.0
Blast furnace (Iron)	0.0078	0.0021	0.0651	--	--	0.0260	6.0 to 9.0
Blast furnace (ferromaganese)	0.1563	0.0208	0.5212	--	--	0.1043	6.0 to 9.0
Basic oxygen furnace (semi-wet air pollution control methods)	No discharge of process wastewater pollutants to navigable waters.						
Basic oxygen furnace (wet air pollution control methods)	--	--	--	--	--	0.0104	6.0 to 9.0
Open hearth furnace	--	--	--	--	--	0.0104	6.0 to 9.0
Electric arc furnace (semi-wet air pollution control methods)	No discharge of process wastewater pollutants to navigable waters.						
Electric arc furnace (wet air pollution control methods)	--	--	--	--	--	0.0104	6.0 to 9.0
Vacuum degassing	--	--	--	--	--	0.0052	6.0 to 9.0
continuous casting	--	--	--	--	0.0078	0.0260	6.0 to 9.0

TABLE 18. MAXIMUM THIRTY-DAY AVERAGE EFFLUENT LIMITATIONS GUIDELINES: TEXTILE MILLS(1) FOR JULY 1, 1977 (47)*

Subcategory	BOD_5	TSS	COD	Total Chromium	Phenol	Sulfide
Wool Scouring(2,4)	5.3	16.1	69.0	0.05	0.05	0.10
Wool Finishing(4)	11.2	17.6	81.5	0.07	0.07	0.14
Dry Processing(3)	0.7	0.7	1.4	--	--	--
Woven Fabric Finishing(4)	3.3	8.9	30-	0.05	0.05	0.10
Knit Fabric Finishing(4)	2.5	10.9	30-	0.05	0.05	0.10
Carpet Mills	3.9	5.5	35.1- 45.1	0.02	0.02	0.04
Stock and Yarn Dyeing and Finishing(4)	3.4	8.7	42.3	0.06	0.06	0.12

*Reference 132.

(1) Expressed as $\frac{\text{kg(lb) pollutant}}{\text{t(1000 lb) product}}$ except Wool Scouring as $\frac{\text{kg(lb) pollutant}}{\text{t (1000 lb) raw grease wool}}$ and Carpet Mills as $\frac{\text{kg (lb) pollutant}}{\text{t(1000 lb) primary backed carpet}}$

(2) Oil and grease limitation for Wood Scouring is 3.6 $\frac{\text{kg(lb)}}{\text{t(1000 lb) raw grease wool}}$

(3) Fecal coliform limit for Dry Processing is 400 MPN per 100 ml.

(4) For those plants identified as Commission Finishers, an additional allocation of 100 percent of the guidelines is to be allowed for the 30-day maximum levels.

PRACTICAL APPLICATIONS OF BIODEGRADATION OF ORGANIC INDUSTRIAL WASTES

Several options are available for the treatment of organic industrial waste streams. Physical and chemical pretreatment is an important precursor to secondary treatment systems when there are concentrated waste streams. At the Union Carbide Petrochemical Plant in Texas City, Texas, waste streams are segregated for chemical recovery, incineration, stabilization, and other pretreatment processes. When the waste is so dilute that such processes are no longer economical, it is sent to a secondary biological treatment plant.

An advantage to biological treatment is the degree to which such systems can be adapted to the removal of residual dissolved or colloidal organic contaminants. Where hazardous or toxic organic constituents are present, biological transformations may result in less innocuous compounds; the disposal of such process residues will, therefore, be less restricted. Effluent limitations guidelines research by the EPA (113) defines end-of-process technology for new sources utilizing the best available demonstrated control technology (BADCT) as biological treatment with suspended solids removal via clarification sedimentation, sand, or dual-media filtration.

Conventional Applications

Conventional applications of biological treatment to industrial organic and hazardous wastes include most techniques used for municipal waste treatment, e.g., activated sludge, aeration basins, trickling filters, and stabilization ponds. Table 19 summarizes applications of conventional treatment schemes to various organic industrial wastes, as described in the literature. Summaries of the efficiency and cost of biological waste treatment schemes applied to petrochemical wastes have been prepared (50). Applications of activated sludge, trickling filters, aerated lagoons, and waste stabilization ponds to a variety of organic chemical industries have also been described (47). Operational characteristics of activated sludge systems make them highly amenable to concentrated waste treatment; their popularity is well documented. Nevertheless, loading control and application of predominantly biodegradable wastes to other treatment schemes can also result in acceptable BOD and COD removal efficiencies.

Innovative Applications

Innovative applications of biodegradation techniques for treatment and disposal of organic industrial or hazardous wastes are included in the following categories:

- Activated carbon adsoprtion with biological regeneration
- Biological seeding

TABLE 19. APPLICATIONS OF CONVENTIONAL TREATMENT SCHEMES TO VARIOUS ORGANIC INDUSTRIAL WASTES AS REPORTED IN THE LITERATURE

Conventional Processes				
Description or Name	Waste(s) Applied	Removal Efficiency	Cost/Unit Const.	Source Date
Activated sludge (pilot)	Ammonical liquor from coke plant	92% TOC, 65% COD, 30% thiocyamate, 55% cyanide	p. 97-98 in ref.	71 1973
Activated sludge	Pump mill (USSR)	99.3% BOD_5, 91.7% SS		142 1974
Activated sludge (laboratory scale)	Ammonical liquor and other waste streams from coke plant	99.1% phenols & catechols, 99.4% ammonium thiocyanate, 99.0% calcium thiocyanate		7 1967
Activated sludge	Refinery pump & paper pharmaceutical	K values (see table)		4 1972
Activated sludge	C_4-C_6 alcohols Lindane	75% BOD, 63% COD		161 1974
Activated sludge plant	Propylene glycol wastewaters	90% TOD	p. 132 (estimates only) in ref.	168 1971
Activated sludge plant	PVC production plant wastes	97% BOD in aer. system		52 1971
Activated sludge, Aerated lagoon, Trickling filter	Categories B, C, & D			113 1974
Activated sludge, Aerated basins, Ditch aeration, Rotating biosurfaces, Trickling filters	Pulp, paper, paperboard, mill wastes			144 1976
Activated sludge	General petrochemical			50 1970
Trickling filters	"			50 1970
Aerated lagoons	"			
Stabilization ponds	"			

TABLE 19 (continued)

Conventional Processes

Description or Name	Waste(s) Applied	Removal Efficiency	Cost/Unit Const.	Source Date
Aerated stabilization basin, Non-aerated stabilization basin, Activated sludge, Trickling filter,	Pulp and paper, industry effluents	BOD 87% SS 84% for ASB and AS		102 1974
Biofiltration, Aerated lagoon, Stabilization pond	Chlorophenolic wastes	82% BOD 94% phenols 65% phenoxy-acids	p. 87 in ref.	74 1971
Activated sludge	Parathion 2,4-D wastewater (up to 900 ppm)			
Anaerobic Digestion	malathion -BHC chlorinated HC's	95% lindane in 2 days		
Trickling filter	Herbicides	76% BOD, 62% phenols		9 1972
Extended aeration	2,4-D, 2,4,5-T (diluted 30 to 1 with municipal -BHC	94% chlorophenols in 2 weeks		
Air floatation to aeration basin	Synthetic rubber laytex wastewater	85% BOD, 85% SS (p. 78)	p. 85-88 in ref.	82 1973
Activated sludge Aerated stabilization basins, Ditch aeration, Rotating biological surfaces, Trickling filters	Pump and paper milling process effluents		p. 453-554 in ref.	156 1976
Activated sludge, Trickling filter, Aerated lagoon, Aerobic-facultative penels	Refinery, drinking pharmaceutical, kraft & sulfite, paper, ammonia still, black liquor, paperboard textile, chemical			39 1966

- Fluidized-bed bioreactor
- Fixed activated sludge
- Deep tank extended aeration
- Activated carbon addition
- Pure oxygen systems
- Deep shaft aeration
- Limited aeration
- Cooling tower bio-oxidation
- Automation/optimization.

Each of these applications is included in one of the following categories:

- Innovative bioreactor design (inherent innovation)

- Innovative accessories (external innovation) - often applied to otherwise conventional treatment schemes

- Innovative operational methods.

A summary of applications, as reported in the literature, is shown in Table 20. The reported removal efficiency for various constituents, as well as retention time for each process and average flow rate is presented in this table.

Innovative Bioreactor Design--

There are several desirable goals in altering or deriving new designs for the waste treatment bioreactor unit. Two of these are:

- Enhanced oxygen transfer to the microbiological cells
- Enhanced contact between wastes and microbiological cells.

There are, of course, benefits to be derived from accelerating the biodegradation process: operational costs may be reduced; less space may be required, resulting in decreased land costs; and greater removal efficiencies can be effected.

Another goal to be considered in the design of innovative biological treatment systems for concentrated industrial or hazardous wastes is the minimization of the toxic effects of certain constituents upon the unit microbial population. Aeration basins, for example, have been designed with long retention times and complete-mix flow characteristics. However, recent surveys of industrial waste treatment techniques (50) have shown that proper pretreatment, the use of surge tanks or lagoons, and process contorl and housekeeping at source plants can have a significant impact on treatment plant efficiency and stability.

TABLE 20. APPLICATIONS OF INNOVATIVE TREATMENT SCHEMES TO VARIOUS ORGANIC WASTES AS REPORTED IN THE LITERATURE

Process name	Waste(s) applied	Removal efficiency	O&M costs/ unit constituent removed	Approx. capital cost/yr	Avg. flow	Bioreactor Retention time	Approx. Influent mg/ℓ	Source data	Category*
Activated carbon: anaerobic regeneration	Textile wastes	49.4% BOD 47.1-56.9% COD 42.4-49.5% TOC (includes pre-equalization)	--	--	378,500 ℓ/day	7-10 min (AC only)	500 BOD 1800 COD 600 TOC	123/1973	B
Activated carbon: aerobic regeneration	Textile wastes	75% COD (theoretical 1 MGD plant)	0.2¢/lb	$550,000 (1971)	3.79×10^6 ℓ/day	1.1 hr	800 1600 mg/ℓ COD	134/1971	B
Biological seeding, pure oxygen, activated sludge	Herbicide orange	up to 77% degraded (by GC)	--	--	Batch	16 days	1380 (herbicide)	164/1974	B
Fluidized bed bioreactor (bench application)	Coal conversion effluent (H_2S, Ammonia, phenols, thiocyanate)	See Table (in text)	--	--	391-505 ml/min	1-3 min	20-140 (phenol)	141/1975	A
Fixed activated sludge (pilot) (also use of biological seed)	Munitions manufacturing wastes (ethyl alcohol, diethyl ether, DNT)	69% BOD 67% TOC 50% COD	--	--	2.4 liters per hour	8 hr	600-1375 TOC	167/1972	B

TABLE 20 (continued)

Process name	Waste(s) applied	Removal efficiency	O&M costs/ unit constituent removed	Approx. capital cost/yr	Avg. flow	Bioreactor Retention time	Approx. Influent mg/ℓ	Source date	Category*
Deep tank extended aeration	Refinery storm runoff ballast water	94% BOD 84% SS	0.11/kg 0.15/kg	2,000,000/ 1973	11-18.9 x 10^6 ℓ/day	19 hr	130 mg/ℓ	135 1974	A
Activated carbon addition	Petrochem +10% sanitary	Approx. 90% BOD	$0.26- 1.21/lb	--	3.79 x 10^5 ℓ/day	--	1700 BOD 3200 COD 2500 MLVS	1 1974	B
Pure oxygen activated sludge	Pulp and paper							156 1976	A
Pure oxygen UNOX								56	
Deep shaft aeration	Textile petrochem	89% BOD 84% SS			150,000 IGPD	35 min	140	21 1976	A
Deep shaft aeration	Chemical	97% BOD		$2.5 mil/76	1.55 x 10^6 ℓ/day	1 day	16900	19 1976	A
	Pharmaceutical	89% BOD		$2.5 mil/87	5.7 x 10^6 ℓ/day	4.3 hr	3000		
	Wood pulp	79% BOD		$1.9 mil/76	8.7 x 10^6 ℓ/day	2 hr	2300		

TABLE 20 (continued)

Process name	Waste(s) applied	Removal efficiency	O&M costs/ unit constituent removed	Approx. capital cost/yr	Avg. flow	Bioreactor Retention time	Approx. Influent mg/ℓ	Source date	Category*
Series lagoons anaerobic -	Petrochemical dilute	88-92% BOD	.18¢/kg BOD	$0.5 mil/81	1.9×10^6 ℓ/day	Approx. 20 days (entire system)	800 BOD	66 1972	A
aerobic -			.044¢/kg BOD	$2.2 mil/71	3.79×10^7 ℓ/day				
facultative			.035¢/kg BOD	$4.7 mil/71	9.5×10^7 ℓ/day				
Anaerobic stabilization to aeration basins	Butadiene ethylene oxide phenol cumene polyethylene bisphenol-A	80% BOD	0.06¢/kg BOD	Approx. $3 mil.	1.6×10^7 ℓ/day	15 days	1400 BOD	59 1973	A
Anaerobic stabilization and aerobic-anaerobic ponds	Chemical paper textile	89% BOD 50% BOD 44% BOD	--	--	--	65 days 18.4 days 3.5 days	--	39 1976	A
Cooling towers	Refinery-dilute	80% BOD 98% phenol	(survey)	(survey)	(survey)	--	--	50 1970	B
Wet composting with biological growth	Acetibem phenol p-cresol, di-Test-butyl-p-cresol dicumyl-peroxide	92-97% BOD 100% volatile acids							

TABLE 20 (continued)

Process name	Waste(s) applied	Removal efficiency	O&M costs/ unit constituent removed	Approx. capital cost/yr	Avg. flow	Bioreactor Retention time	Approx. Influent mg/ℓ	Source date	Category*
Automation/ optimization nutrient addition	Glycol wastes	(Technology descriptions only)	--	--	--	--	--	169 1975	C
F/m control floc control biological inhibitor detector (pilot)									

* Category:

A = Innovative bioreactor design (inherent innovation) or additional biological stages
B = Innovative accessories
C = Innovative operational methods

Deep Shaft Aeration--Systems designed around a plug flow concept also utilize increased oxygen transfer with pressure to eliminate short circuiting and to enhance biological degradation (19, 21). Experimentation with U-tube aeration for sanitary sewer systems indicated that this process has low land and operational costs and can be installed without problems in relatively unstable soil with a high groundwater level (110). A variation on the U-tube process is known as deep shaft aeration (Figure 7). Such systems, which include sufficient retention time for bioconversion, are successfully treating textile, petrochemical, pharmaceutical, and wood pulp process wastes in the United States, Canada, the United Kingdom, and Germany. Typical operating conditions and plant efficiencies for a deep-shaft aeration plant are shown in Table 21.

Pure Oxygen Applications--Pure oxygen systems are innovative bioreactor designs that can enhance oxygen transfer into the aqueous phase. The most widely applied form of this technology in both pilot and full-scale treatment plants is a pure oxygen-activated sludge system. The use of high purity oxygen for oxygenation of pulp, paper, and paperboard milling wastes has been successful (156).

It is reported that closed activated-sludge plants can operate at very high active sludge levels (5,000 to 7,000 mg/ℓ), and dissolved oxygen concentrations (greater than 5/mg/ℓ), and with high overall utilization of oxygen feed gas (greater than 90 percent), frequently reducing BOD_5 levels to less than 30 mg/ℓ. As in the deep shaft process, the quantity of secondary sludge produced at the mill plants is reported to be less than is generated by conventional activated sludge. Moreover, it can be successfully concentrated with minimal conditioning.

Figure 8 is a schematic diagram of a Union Carbide Corporation UNOX pure oxygen activated sludge system. Oxygen gas is fed in during the first stage at a pressure slightly greater than ambient. Recirculating gas blowers in each of the three unit stages pump oxygen to a rotating sparger; pumping action of the impellers located on the same sparger shafts maintain longer residence time for the gas bubbles. Gas is usually recirculated within a stage at a higher rate than the rate of gas flow from one stage to another. The rate of gas transfer is controlled by the oxygen demand in each. Each stage is covered to contain the oxygen and off-gases (chiefly CO_2 and N_2).

Although the cost of energy for mechanical oxygen diffusion is greatly reduced compared to conventional air systems, some of these savings are negated by the energy required to produce the pure oxygen supply. Nevertheless, within a range of process scales, savings will outweigh the additional cost of oxygen production hardware and operation. This range of cost-effectiveness is further dictated by the quality and constituents of the waste stream.

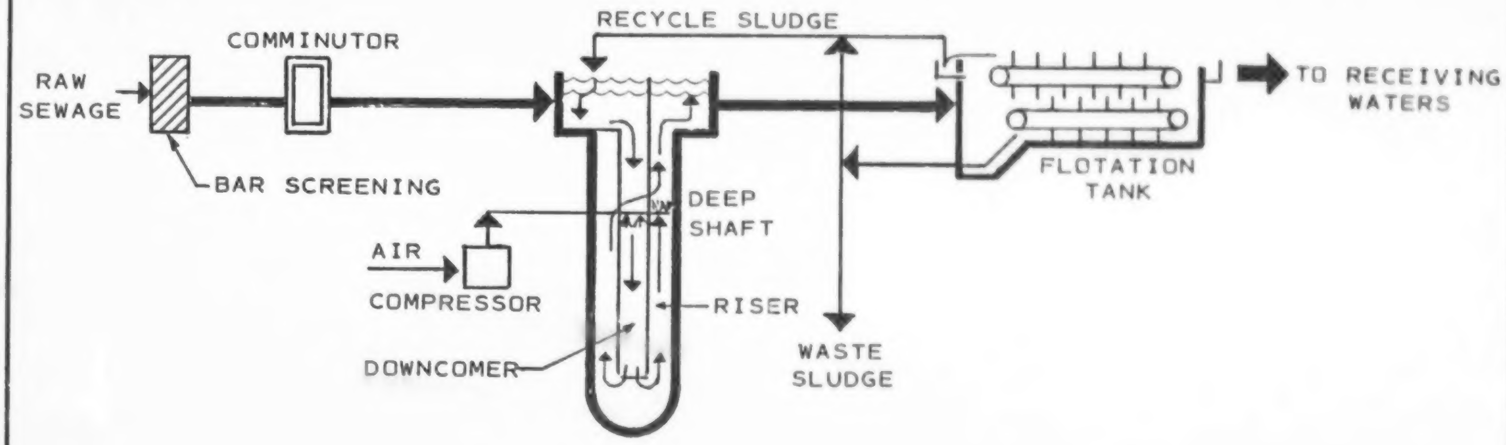

RAW SEWAGE
COMMINUTOR
BAR SCREENING
RECYCLE SLUDGE
AIR
COMPRESSOR
DEEP SHAFT
RISER
DOWNCOMER
WASTE SLUDGE
FLOTATION TANK
TO RECEIVING WATERS

Figure 7. Example of a deep shaft aeration plant treatment scheme.

TABLE 21. OPERATING CONDITIONS AND PLANT EFFICIENCIES FOR A DEEP SHAFT AERATION PLANT

Raw sewage food (IGPD)	150,000
Shaft residence time (min.)	35
MLSS (mg/ℓ)	6,000
Daily BOD load (kg/day)	484
F/M ratio (day^{-1})	1.4

	Average Concentration (mg/ℓ)
Inlet	
BOD_5	140
Suspended Solids	190
Outlet	
Whole BOD_5	15
Filtered BOD_5	5
Suspended Solids	30

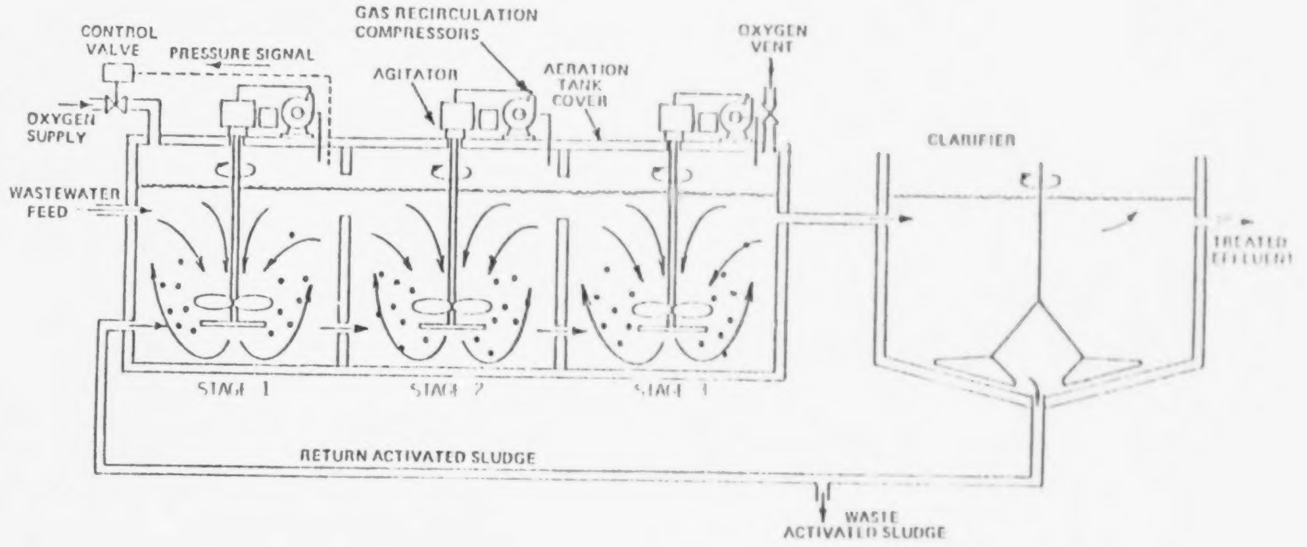

CONTROL VALVE
PRESSURE SIGNAL
OXYGEN SUPPLY
GAS RECIRCULATION COMPRESSORS
AGITATOR
AERATION TANK COVER
OXYGEN VENT
WASTEWATER FEED
CLARIFIER
TREATED EFFLUENT
STAGE 1
STAGE 2
STAGE 3
RETURN ACTIVATED SLUDGE
WASTE ACTIVATED SLUDGE

Figure 8. Schematic diagram of three-stage UNOX system.

On-site oxygen production for pure oxygen-activated sludge is not only feasible but is being practiced on a full-scale basis. High pressure molecular sieve systems are used to separate oxygen and nitrogen, producing a relatively pure oxygen source. For larger scale plants, cryogenic air separation processes are often applied: the liquefaction of the air is followed by fractional distillation separating the air into oxygen and nitrogen components (55). If there is a process ozonator-contactor-decomposer at the plant, oxygen may also be derived from the destruction of exhaust ozone. Wastewater treatment using conventional air-activated sludge has been compared with treatment using pure oxygen-activated sludge at both pilot and full-scale plants (85). The reported advantages of the pure oxygen method relate to sludge quality, sludge production, required detention time for treatment, and economies of scale. A comparison of process design conditions for the two technologies is shown in Table 22.

It is also reported that the UNOX system has good process stability when exposed to peak loading or shock loading, because of the higher dissolved oxygen (DO) maintained in the bioreactor unit (53).

Studies of the treatment of petrochemical wastewaters using the UNOX process have been documented. Further comparisons between the UNOX and conventional air-activated sludge systems are shown in Table 23. The data are based upon a hypothetical petrochemical wastewater with an average flow of 6 MGD, a peak flow of 6.25 MGD, and the following characteristics:

Parameter	Average	Peak
Sewage Temperature, °C	95	95
BOD_5 Concentration, mg/ℓ	1,000	1,240
kg/day (lb/day)	110,000 (242,500)	142,153 (313,400)
COD Concentration, mg/ℓ	2,500	3,100
kg/day (lb/day)	275,000 (606,300)	355,384 (783,500)
SS Concentration, mg/ℓ	150	150
kg/day (lb/day)	16,500 (36,380)	17,160 (37,830)
pH	7.0	7.0

A summary of treatment efficiencies for various petrochemicals and wastes using the UNOX system is shown in Table 24.

Deep tank aeration--Deep tank extended aeration is practiced at an Atlantic Richfield refinery in East Chicago, Indiana, which produces aqueous wastes from a variety of refinery operations (135). Combined refinery wastewater and surface runoff water averaging 19,000 m^3/day (5 MGD) is initially treated in API-type

TABLE 22. COMPARISON OF PROCESS DESIGN CONDITIONS FOR THE "UNOX" SYSTEM AND FOR CONVENTIONAL AIR AERATION SYSTEMS FOR TYPICAL MUNICIPAL WASTEWATER

	"UNOX" Oxygenation System	Conventional Air Aeration Systems
Mixed Liquor D.O. Level - mg/ℓ	4-8	1-2
Aeration Detention Time (raw flow only) - hr	1-3	3-8
MLSS Concentration - mg/ℓ	4,500-8,000	1,000-3,000
MLVSS Concentration - mg/ℓ	3,500-6,000	900-2,600
Volumetric Organic Loading - kg/1000 m^3	2,400-4,000	480-960
Food/Biomass Ratio - kg BOD/kg MLVSS	0.4-1.0	0.2-0.6
Recycle Sludge Ratio - kg recycle/kg feed	0.2-0.5	0.3-1.0
Recycle Sludge Concentration - mg/ℓ	15,000-35,000	5,000-15,000
Sludge Volume Index (Mohlman)	30-70	100-150
Sludge Production - kg VSS/kg BOD removed	0.4-0.55	0.5-0.75

TABLE 23. "UNOX" VS CONVENTIONAL AIR ACTIVATED SLUDGE (56)

	UNOX System	Conventional Air System
OPERATING POWER BHP		
Oxygen dissolution	450	1,990
Oxygen generation*	678	--
	1,128	1,990
INSTALLED POWER, NHP		
Oxygen dissolution	510	2,250
Oxygen generation	900	--
	1,410	2,250
ENERGY REQUIREMENTS		
Total operating KW	911	1,648
Total yearly KWH x 10^{-3}	7,980	14,436
EFFICIENCY		
Dissolution transfer efficiency (lbs O_2 diss./BHP-hr)	5.42	1.52
System transfer efficiency (lbs O_2 diss./BHP-hr)	2.16	1.52
Overall transfer efficiency (KWH/lb O_2 diss.)	0.35	0.55
CAPITAL COST		
Aeration tankage	803,550	1,848,110
Clarifiers	355,790	387,600
Installation, location, overhead, etc.	532,290	996,250
Engineering	109,800	209,000
Contingency	270,000	516,000
Oxygen plant installation	310,000	--
Oxygen dissolution and generation equipment	2,000,000	829,000 (only diss.)
TOTAL SYSTEM COST	$4,381,630	$4,785,960

Source: 50.

*Monthly average generation power.

TABLE 24. SUMMARY OF "UNOX" SYSTEM EXPERIENCE WITH CHEMICAL AND PETROCHEMICAL WASTES

Location	Type Study	Type of Waste	BOD Applied mg/ℓ	BOD F/M day-MLVSS	Percent BOD Removed
Tenneco Chemicals, Houston, TX	Pilot Plant	Acetylene	203	0.54	82
Union Carbide Corp., Tait, LA	Pilot Plant	Various	3,063	0.86	76
Hercules, Inc., Wilmington, NC	Pilot Plant	Acetic & Formic Acids	1,496	0.20	97
Exxon, Baton Rouge, LA	Pilot Plant	Low weight acids & alcohol	452	0.75	81
DuPont, Chambers Works, NJ	Pilot Plant	Various	278	0.37	91
Ciba Geigy, Cranston, RI	Pilot Plant	Specialty Chemicals	1,006	0.34	86
Chemagro, Kansas City, KS	Pilot Plant	Pesticides	554	0.49	90
Shellberre, France	Pilot Plant	Various	625	0.28	96
Bayer (Elberfeld) Germany	Pilot Plant	Various	1,797	0.63	98
Ciba Geigy, Switzerland	Pilot Plant	Dyes	1,064	0.86	89
Union Carbide, Montreal, Canada	Pilot Plant	Petrochemical	484	0.72	86
Union Carbide, Sistersville, WV	Full Scale	Organosilicones	450	.5-1.5	92
Mitsubishi (Kasei) Japan	Treatability	Ethylene Cracker	2,310	0.48	96 (soluble)
Mitsutuat (Osaka) Japan	Treatability	Various	1,160	0.57	97 (soluble)
Sumitono Niihaka, Japan	Treatability	Methionine W.W.	1,366	0.51	95 (soluble)
Fuji Film (Odawara) Japan	Treatability	Alcohols	3,570	0.63	99 (soluble)
Kyowa Yuka Yokkaichi, Japan	Treatability	Acetaldehyde	1,144	0.52	94 (soluble)
Oasaka Gas, Japan	Treatability	Refinery	650	0.63	94 (soluble)
Union Carbide, Antwerp, Belgium	Treatability	Ethylene oxide production	2,400	0.17	99
Shell, Rotterdam, Holland	Treatability	Various	830	0.74	90
Napthachimie, France	Treatability	Petrochemical	928	0.52	94
Lachema, CSSR	Treatability	Citric Acid	13,560	0.47	97
Hoechat, Germany	Treatability	Petrochemical	1,293	1.10	80
Sandox, Switzerland	Treatability	Pharmaceutical	1,060	0.80	94
Shell, Norco, LA	Treatability	Various	969	0.52	97
Union Carbide, Brownsville, TX	Treatability	Acetic & Formic Acid	4,967	1.58	98

oil/water separators before introduction into the deep tank system. The deep tank aeration basins are followed by secondary clarification. The process flow is split in half and delivered to two bioreactors operating side by side, each 36.6 m (120 ft) in diameter with a 7.3 m (24 ft) water depth. Aeration is accomplished by two aerators in each tank. Air is supplied to the system by centrifugal blowers. There are three 250-hp (187 kw) blowers, two normally in operation and one on standby. The design air rate of the two bioreactors is 159 m^3/min for each tank.

Complete mixing in such systems is usually maintained by air diffusers, baffles, draft tubes, and other mechanisms. Operating experience at this refinery indicated a removal efficiency of 94 and 84 percent for BOD and supended solids, respectively. The yearly operating cost for processing 6.4 billion ℓ/yr of refinery wastewater was $80,820, resulting in a unit cost of $12.40/million ℓ of wastewater processed. The utilities cost was approximately $44,400/yr, maintenance $28,765/yr (high because of startup costs), and operating labor $7,665/yr.

In this particular deep tank system, upset of the biomass by toxins or corrosives never resulted in complete curtailment of the operation. Experience also demonstrated that the system is capable of achieving effluent criteria when hydraulically or organically overloaded and is capable of treating variable waste loads produced during normal refinery operations.

Laboratory studies of deep tank aeration (55) also indicate that this type of innovative bioreactor design has potential. Some of the areas in which potential capital savings can be achieved with deeper tanks are:

- Less connected horsepower and blower capacity
- Fewer diffusers and less air distribution piping
- Less land and ancillary equipment such as distribution and collection channels, return sludge systems, monitoring, control and froth spray systems, walkways, and other related structures. Probable savings in operating costs include: less power, equipment and facility maintenance, and lower interest and replacement costs. However, excessive tank depths may interfere with adequate mixing. Under such conditions, the air required for mixing may exceed that required for transfer and dispersion forces may inhibit floc formation.

Fluidized-bed bioreactors--Both the tapered fluidized-bed reactor and the fixed activiated-sludge processes described below utilize microorganisms adhering to some type of solid media in the bioreactor chamber. Several examinations of the effects of solid surfaces upon microbial activity have been conducted (61, 172). Under experimental conditions, it has been shown that surfaces enable bacteria to develop in substrates otherwise too dilute for growth. Development occurs in the form of epiphytic slime or colonial growth. Enhanced COD and BOD removals have been attributed to the presence of biologically active slimes. In addition, some bacteria are actively sessile, attaching themselves to surfaces during the early logarithmic phase of growth rather than during later growth phases. It has been suggested that food particles are more available to cells on solid surfaces where the interstices at the tangent of the bacterial cell and the solid surface retard the diffusion of exoenzymes and hydrolyzates away from the cell. Inert materials that support microbes in the bioreactor in continuous fermentation processes also tend to prevent the loss of microbes with removal of spent liquor, making heavy loading of fresh substrates possible.

Tapering of the fluidized bed containing anthracite coal would probably expand the range of optimum operation conditions (141). Otherwise, it would be difficult to maintain nonfluctuating operating conditions, since there are frequently high bed expansion and low stability. However, in a tapered reactor, if the cross section of the entry zone is sufficiently small and expansion is gradual, the flow profile throughout the reactor will be uniform and have fewer eddies.

A bench-scale fluidized reactor is operable under varying conditions of air or oxygen addition (Table 25). Gas is applied at the column bottom or to the feed waste stream. Under ideal conditions and using a mutant strain of pseudomonas, the bench-scale fluidized bed is very efficient in the removal of phenol.

Bench-scale experiments with the degradation of phenolic waste by fluidized-bed bioreactors has also been reported by Holladay (64).

Anaerobic digestion-equalization--Several full-scale treatment schemes utilizing anaerobic stages have been described in the literature and are shown to be effective in petrochemical waste processing.

The ecological relationships in anaerobic processes can be complex. In lagoon systems, there is a large surface area to volume ratio; substantial amounts of oxygen can be introduced into the near-surface waters by infusion or wind mixing. Many anaerobic primary treatment stages are operated as parallel fill and draw basins, and some infiltration of liquid wastes into the soil may occur. Natural bacterial activity, primarily anaerobic and facultative, stabilizes the organic matter in the stored wastewater through conversion and stabilization (Figure 9). The favoring of anaerobic conditions minimizes production of cell mass.

TABLE 25. PHENOL DEGRADATION RATES IN TAPERED FLUIDIZED BED BIOREACTOR (141)*

Feed Stream**		Effluent Phenol Concentration† ppm	Reactor Conversion Rate‡ g/day/ℓ	Method of Oxygenation
Flow Rate mℓ/min	Phenol Concentration ppm			
409	14	0.05	2.4	Air sparge in column
425	38	<1	6.6	Air sparge in column
412	140	100	6.9	Air sparge in column
475	9	<0.025	1.6	Feed stream saturated with O_2 at ambient pressure
480	17	.050	3.0	Feed stream saturated with O_2 at ambient pressure
482	20	.050	3.9	Feed stream saturated with O_2 at ambient pressure
500	35	<1	6.6	Feed stream saturated with O_2 at ambient pressure
505	31	10	6.6	Feed stream saturated with O_2 at ambient pressure
374	30	<0.025	4.6	Feed stream saturated with O_2 at 40 psig
388	58	<0.050	9.3	Feed stream saturated with O_2 at 40 psig
391	63	0.50	10.2	Feed stream saturated with O_2 at 40 psig

---

*All runs were made at ambient pressure, 25 ± 2°C, pH 7.0-7.2.

**In all tests, recycle effluent was used with a primary feed stream containing 450 to 4,800 ppm of phenol.

†Most sensitive assays of less than 1 ppm had a sensitivity of 0.025 ppm. The less sensitive assay had a sensitivity of 1 ppm.

‡Included the volume of the fluidized bed, as well as the volume of solution above the bed and the volume of the settling chamber.

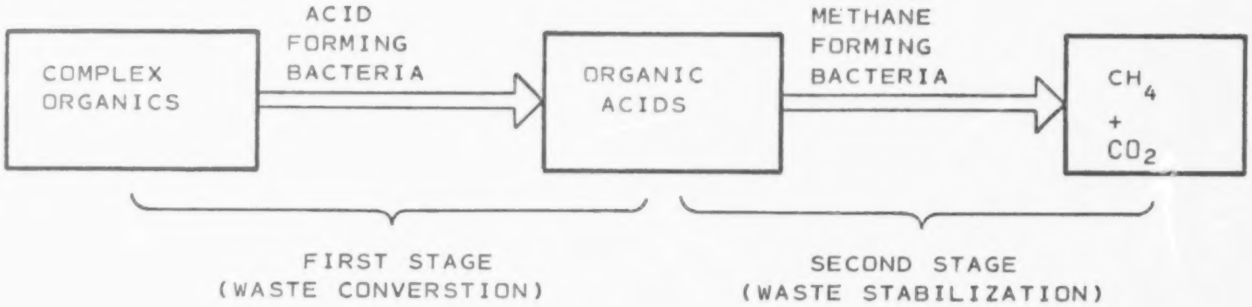

COMPLEX ORGANICS
ACID FORMING BACTERIA
ORGANIC ACIDS
METHANE FORMING BACTERIA
$CH_4 + CO_2$
FIRST STAGE (WASTE CONVERSTION)
SECOND STAGE (WASTE STABILIZATION)

Figure 9. Two stages of anaerobic waste stabilization (100).

McCarty (100) indicates that the design parameters and process limitations of anaerobic treatment are dependent upon the microbial and biochemical components. Intermediate acid formation is dependent upon facultative and anaerobic bacteria. Litter reduction in BOD is achieved, but acids are formed, and some cell material is generated. It is primarily the methane-forming bacteria that stabilize the oxidizable organics. Sixteen grams of methane evolved from the stabilization of a given waste correspond to the removal of 64 g of ultimate BOD or COD. The variety of symbiotic and competing biological and abiotic reactions that characterize an anaerobic treatment lagoon is shown in Figure 10.

As indicated by Hovious et al. (65), anaerobic digestion-stabilization is particularly effective in treating some petrochemical waste components such as low-molecular-weight acids and alcohols. Such materials may enter the two-stage fermentation process and be directly converted to methane. Destruction of the acids by methanogenic and photosynthetic purple sulfur and non-sulfur bacteria helps maintain an acceptable pH in the biological treatment steps.

Another important phenomenon closely related to anaerobic fermentation of waste materials is the sulfur cycle. A variety of bacteria utilizes the sulfate materials in wastes as an electron donor during the oxidation of organic materials. Desulfovibrio desulfuricans performs such a reduction of sulfates. The H_2S produced by the reduction of sulfate or other sulfur-containing materials is the cause of the "rotten egg" odor occasionally associated with anaerobic treatment. However, biochemical and abiotic chemical reactions occurring under anaerobic or aerobic conditions work to control odors by utilizing the sulfide materials. If oxygen is introduced to previously anaerobic zones, autoxidation of sulfides may occur. Bacteria of the family thiobacteriacae are chemosynthetic organisms that can oxidize sulfide compounds or elemental sulfur to sulfate, but, with few exceptions, are aerobic. Bacteria of the family thiorhodaceae, capable of producing bacteriochlorophyll, are anaerobic or microaerophilic. Their photosynthetic metabolism utilizes reduced sulfur compounds such as hydrogen sulfide to serve as the hydrogen donor during the reduction of CO_2. This form of biooxidation of sulfides usually results in the production of elemental sulfur droplets inside the individual bacterial cells.

Work by Hovious et al. at two full-scale anaerobic lagoons treating petrochemical wastes indicates that lagoon performance is correlated with volumetric-organic loading and temperature (65). Monitoring with gas-liquid chromatograph showed removal of specific organic materials (Table 26). Two lagoon loading rates were evaluated, one with a concentrated waste (15,000 mg/ℓ COD) and one with dilute waste (1,500 mg/ℓ COD). The more lightly loaded lagoon treating concentrated waste showed a lower effluent

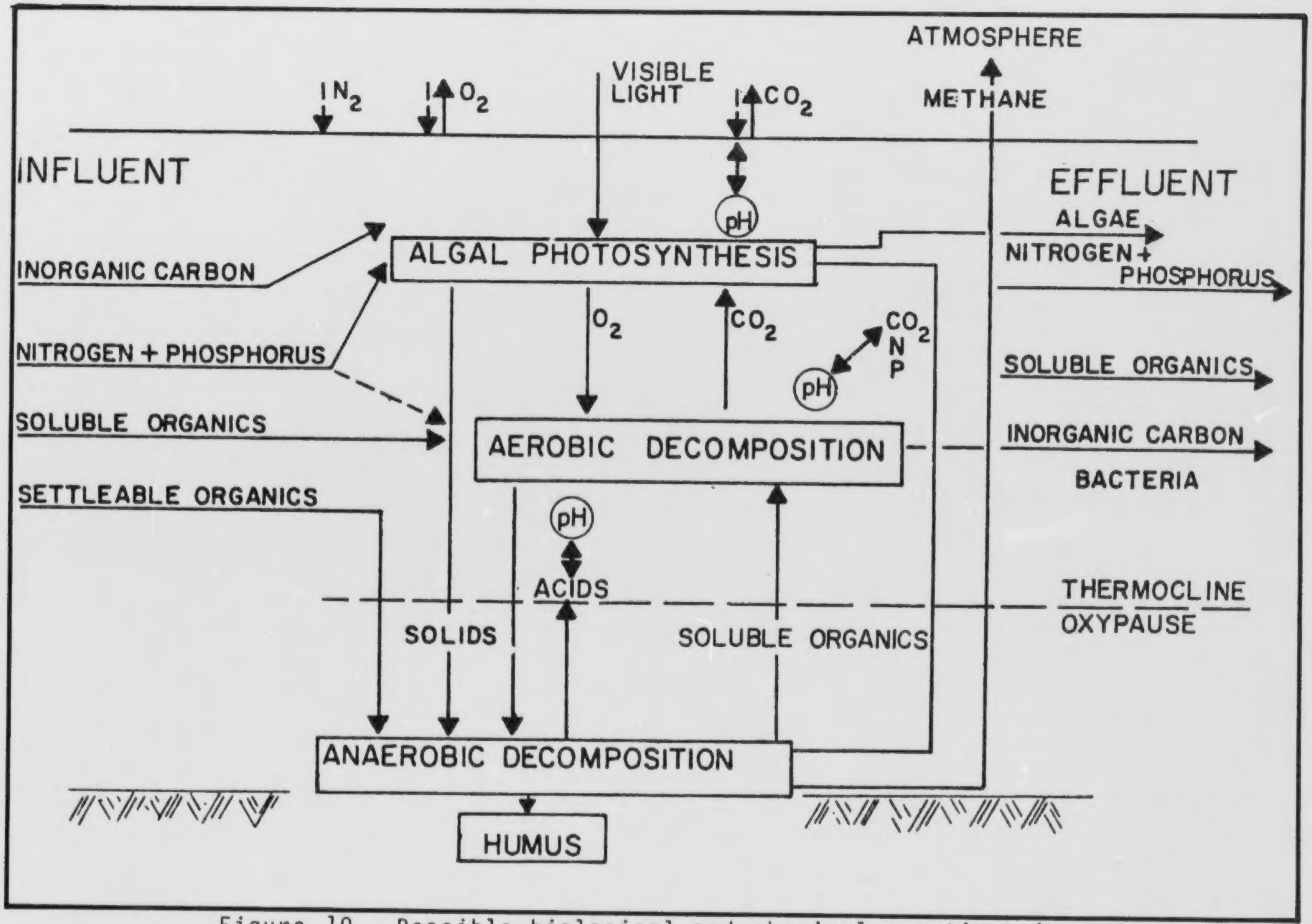

ATMOSPHERE
VISIBLE LIGHT
N_2
O_2
CO_2
METHANE
INFLUENT
EFFLUENT
pH
INORGANIC CARBON
NITROGEN + PHOSPHORUS
SOLUBLE ORGANICS
SETTLEABLE ORGANICS
ALGAL PHOTOSYNTHESIS
O_2
CO_2
CO_2 N P
pH
AEROBIC DECOMPOSITION
pH
ACIDS
SOLIDS
SOLUBLE ORGANICS
ANAEROBIC DECOMPOSITION
HUMUS
ALGAE
NITROGEN + PHOSPHORUS
SOLUBLE ORGANICS
INORGANIC CARBON
BACTERIA
THERMOCLINE
OXYPAUSE

Figure 10. Possible biological and chemical reactions in anaerobic treatment lagoon processes.

TABLE 26. REMOVAL OF SPECIFIC ORGANICS IN ANAEROBIC LAGOONS*

	Dilute Wastes, 208.6 kg/day/1000 m^3			Concentrated Wastes	
Compound	Influent (mg/ℓ)	Effluent (mg/ℓ)	Influent (mg/ℓ)	353 kg COD/1000 m^3 Effluent (mg/ℓ)	770 kg COD/1000 m^3 Effluent (mg/ℓ)
Methanol	80	35	380	135	145
Ethanol	80	15	270	120	130
n-Propanol	--	--	170	35	40
Isopropanol	60	30	175	45	55
n-Butanol	--	--	170	75	80
Isobutanol	--	--	250	80	85
n-Pentanol Isopentanol	--	--	315	70	100
Hexanol	--	--	140	20	30
Acetaldehyde	30	10	80	35	40
n-Butyraldehyde	--	--	190	50	35
Isobutyraldehyde	--	--	210	50	50
Acetone	90	60	150	80	70
Methyl ethyl ketone	10	5	--	--	--
Benzene	10	5	--	--	--
Ethylene glycol	135	30	755	155	190
Acetic acid	215	220	2,120	2,280	2,620
Propionic acid	--	--	0	505	470
Butyric acid	--	--	0	330	300

*Data are averaged from 5 to 12 occurrences in grab or composite samples.

Note: 1b/day/1000 cu ft x 16 = g/day/cu m.

concentration of constituents detected in the raw waste than the heavier loaded lagoon. In experiments with pilot and full-scale lagoon treatment of industrial organic wastes, it was also found that optimum performance was at temperatures between 20° and 43°C (60). Specific performance data for lagoons where volume varied from 0.19 to 1,700 m^3 are presented in Table 27. The anerobic-aerated-facultative lagoon scheme is also reported to have economic advantages over conventional, completely mixed, activated sludge. The anerobic-aerated stabilization system will produce an effluent comparable to the activated-sludge plant; a significant reduction in unit removal cost is also typical. However, high land requirements and reduced efficiency at lower temperatures are some of the negative aspects of the scheme.

Construction costs for plants with daily flows of 1.9 (0.5), 3.8 (10.0), and 9.5 (25.0) x 10^4 m^3/day (MGD) are shown in Table 28. A waste strength of 800 mg/ℓ BOD was selected for the base case estimate (66). The operational costs given in Table 29 are for the same lagoon systems. Capital and operational costs for a Union Carbide lagoon-type treatment system in Puerto Rico have also been derived (59).

Innovative Accessories--

Fixed activated sludge (FAS)--Kato and Sekikawa first described the application of the fixed activated sludge (FAS) biological treatment process to industrial wastes (81). An application of the treatment process to munitions-manufacturing waste is described in Albert et al. (4).

The FAS process was first devised to overcome bulking problems caused chiefly by the growth of filamentous microorganisms in wastes from an octanol plant and a soft drink manufacturing plant. Screens are inserted in the conventional activated-sludge bioreactor to provide a substrate for sessile filamentous species and to prevent excessive suspended biological solids carry-over into the secondary clarifiers. In applying the system to munitions wastes, researchers observed that the waste stream (primarily ethyl alcohol, diethyl ether, and DNT) promoted growths of filamentous microorganisms in the receiving streams. The decision to utilize the FAS approach was a result of these observations. In pilot investigations, substrate removal efficiency in terms of TOC, BOD, and COD was 81, 76, and 76 percent, respectively, when the TOC was in the neighborhood of 100 mg/ℓ. The operating F/M ration was 0.60 and the calculated k value or removal rate was 0.90 hr^{-1}. The effect of the screen area was also evaluated; it was reported that the screen area was limiting when the influent TOC concentration was greater than 100 mg/ℓ. It was concluded that if a fixed activated-sludge unit is to be designed to treat the particular munitions waste, provisions for increasing the screen area available for colonization will enable the operation of the system at higher organic concentrations, and

TABLE 27. DATA FROM UNION CARBIDE PILOT AND FULL-SCALE STUDIES

Lagoon	Volume, m^3	Temperature, ^oC	Waste Strength, mg/ℓ		Volumetric Loadings, kg/1000 m^3		Areal Loading, kg/A-day		Removal %	
			BOD	COD	BOD	COD	BOD	COD	BOD	COD
Texas City Plant	9.84×10^4	--	4510	8450	151.8	278.9	302	545	33	30
		--	4440	8440	144.7	278.9	290	545	39	31
		--	5500	--	105.9	--	209	--	58	--
Texas City Plant	4.2×10^5	--	2990	5900	14.1	27.2	60	119	66	46
		--	2685	5960	12.5	27.2	55	120	63	42
		--	2280	4450	19.0	35.3	80	154	65	29
Seadrift Plant	6.8×10^5	28	536	--	12.0	--	60	--	75	--
		22	527	--	14.5	--	73	--	75	--
		16	598	--	17.7	--	85	--	69	--
		24	547	--	22.6	--	108	--	76	--
		29	641	--	20.8	--	104	--	83	--
Texas City Plant	0.189	27	--	1360	--	141.2	--	436	--	56
		21	--	1420	--	148.3	--	454	--	50
		31	--	1300	--	134.1	--	418	--	60
		13	--	1310	--	137.7	--	423	--	38
		8	--	1410	--	148.3	--	454	--	30
		30	--	1270	--	134.1	--	409	--	54
		20	--	1385	--	141.2	--	440	--	46
		43	--	1295	--	134.1	--	416	--	48
		48	--	1410	--	148.3	--	452	--	23
		31	--	1240	--	127.1	--	399	--	57
		27	--	1330	--	137.7	--	426	--	43
		20	--	1380	--	144.7	--	443	--	46
		31	--	1245	--	130.6	--	400	--	56

TABLE 27 (continued)

Lagoon	Volume, m^3	Temperature, ^oC	Waste Strength, mg/ℓ		Volumetric Loadings, kg/1000 m^3		Areal Loading, kg/A-day		Removal %	
			BOD	COD	BOD	COD	BOD	COD	BOD	COD
Texas City Plant	5.50*	23	580	1200	60.0	125.2	222.7	463.6	47	24
		30	550	1100	56.5	113.9	213.6	422.7	73	42
		27	490	1230	15.9	128.4	188.6	477.2	76	52
		23	680	1260	70.6	131.6	261.4	488.6	67	53
		28	630	1260	67.1	131.6	254.5	486.3	73	52
		28	--	1620	--	168.5	--	622.7	--	50
		28	1053	2150	225.9	449.3	831.8	1663.6	30	30
		26	1480	1930	190.6	401.1	713.6	1486.4	20	19
		19	1080	2000	113.0	208.3	418.2	770.5	45	37
		15	1080	2160	113.0	225.9	418.2	831.8	48	42
		10	1080	2160	113.0	225.9	418.2	831.8	43	40
		17	925	2160	95.3	225.9	356.8	831.8	54	45
		13	1390	3080	144.7	320.9	534.1	1188.6	34	30
		19	1540	3400	158.9	353.0	594.5	1306.8	40	33
		22	1500	3240	208.3	449.3	772.7	1663.6	52	37
		13	1620	3000	113.0	208.3	415.9	772.7	46	32
		19	1390	3000	95.3	208.3	356.8	772.7	52	37
		22	1050	2300	80.2	158.9	297.5	595.4	68	49
		23	810	1740	113.0	240.7	415.9	890.9	62	45
		28	1040	3020	144.7	417.2	534.1	1545.5	62	38
		29	1230	3080	128.4	320.9	445.0	1188.6	54	42

*Lagoon of an irregular, prismoid shape. Effective depth computed as volume/surface area.

TABLE 28. CONSTRUCTION COST SUMMARY ANAEROBIC-AERATED STABILIZATION SYSTEM (66)*

System Component	Plant Size (10^6 m³/day) 1.9×10^4	3.79×10^4	9.46×10^4
Neutralization			
Structural	$ 6,800	$ 22,000	$ 51,000
Mixing	3,000	9,300	15,500
Reagent Storage	30,400	30,400	60,800
pH Control	12,000	12,000	24,000
Clarification			
Structural	20,700	123,600	279,300
Mechanical Equipment	20,700	59,000	146,000
Anaerobic Ponds			
Earthwork	70,800	326,500	516,500
Concrete Liner	1,900	39,300	104,300
Aerobic Basin			
Earthwork	63,800	209,500	368,300
Concrete Liner	10,000	32,800	77,100
Aeration Equipment	45,000	448,000	900,000
Electrical Support	22,800	85,500	194,000
Facultative Ponds			
Earthwork	36,500	135,500	323,000
Concrete Liner	15,400	59,100	239,000
Piping	38,700	167,400	412,600
Instrumentation	30,000	56,000	115,000
Building and Lab Equipment	34,000	51,000	70,000
Site Preparation	22,000	49,100	93,600
Land at $1,000/acre	9,000	100,000	230,000
Subtotal	$506,000	$2,016,000	$4,220,000
Construction Contingency	51,500	209,000	430,000
Construction Cost	$560,000	$2,225,000	$4,650,000
Cost/lb BOD Applied	168	33	28
Cost/1000 Gal.	1,120	222	186

*1971 dollars.

TABLE 29. ESTIMATED OPERATING COST ANAEROBIC-AERATION STABILIZATION SYSTEM (60)

	Plant Size, 10^6 m^3/day		
	1.9×10^4	5.79×10^4	9.46×10^4
Operating Labor & Supervision			
Technical Supervision	$ 5,800	$ 17,500	$ 17,500
Day-Shift Supervisor	6,200	12,500	12,500
Operators	36,400	72,800	72,800
Laboratory Analysis	5,200	18,000	20,000
Mechanic-Instrument Man	5,200	10,400	15,600
Reagents			
NH_3 - 1 lb N/20 lb BOD	500	10,000	25,000
H_3PO_4 - 1 lb P/100 lb BOD	200	23,800	59,500
H_2SO_4 - 3000 lb - 93% Acid/MM Gal	7,800	150,000	375,000
Power[**]			
Aeration Horsepower x 1.15	11,400	157,000	372,000
Maintenance			
2.0 Percent of Construction Cost	10,000	44,000	80,000
Operating Supplies	300	2,000	4,100
Annual Operating Cost	$ 90,000	$518,000	$1,054,000
Sludge Disposal[†]	20,000	25,000	70,000
Amortize Investment - 20 yrs at 6%	49,000	194,000	405,000
Total Annual Cost	$159,000	$737,000	$1,529,000
Cost/1000 Gallons	0.87	0.21	0.17
Cost/lb BOD Removed	0.14	0.034	0.028
Cost/lb COD Removed	0.081	0.020	0.016

[*] 1971 dollars

[**] Power at $0.01 per kw-hr

[†] Annual operating plus investment costs.

less dilution or less basin volume will be required. It was also noted that secondary clarification for such systems should be designed to minimize wall effects upon the filamentous sludges. SVI values were high and could indicate problems in this regard. Experimental result comparisons of FAS with conventional activated sludge are shown in Table 30 (81) for an octanol plant waste. FAS requires aeration, and the economic advantages or competitiveness with other methods are not well established. The primary advantage is the control of sludge bulking.

Biological regeneration of activated carbon--The use of biological processes for the regeneration of activated carbon employed for chemical treatment of two Rhode Island textile plant waste streams has been mentioned above. Like other biological treatment schemes utilizing solid substrates for enhancement of biochemical reactions, the granular carbon in activated-carbon columns has been observed to enhance biodegradation.

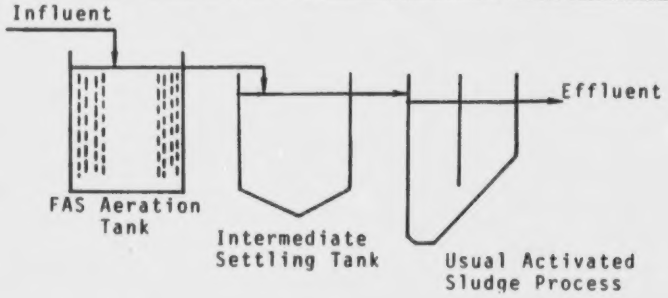
Pilot and full-scale treatment systems described thus far operate in alternating contamination and regeneration phases. During the contamination phase, the textile processing wastes are passed through upflow columns, and organic materials are adsorbed onto the carbon matrix. At one of the Rhode Island sites, anaerobic regeneration was induced by maintaining the columns in periodic quiescent modes. The other site practiced aerobic regeneration by introducing a viable, acclimated, dispersed bacterial culture in an upflow mode. Dissolved oxygen in the culture was maintained at a level greater than 2 mg/ℓ by aerators. Figure 11 shows the schematic diagram for such a system (134).

In full-scale plant operations with anaerobic regeneration, 25 percent soluble TOC was removed in the contamination cycle with an average flow of 3.6 x 10^2 m^3/day (95,100 gal/day). It has been shown that with an average flow of 2.8 x 10^2 m^3/day (74,000 gal/day) and a full 1.83 m (6.0 ft) bed depth, the projected removal could be 35 percent. On each contamination-regeneration cycle, 47 percent of MLVSS or 10.7 kg (23.6 lb) of MLVSS/6-hr treatment cycle was removed, thus reducing the sludge handling problems. Removal of dissolved COD was related to soluble TOC removal and was approximately 13.3 kg (29.3 lb)/treatment cycle. It was further demonstrated that total COD, dissolved COD, and MLVSS can be closely related; the data of one can be used to check against the data of the others. Auxiliary treatment units included removal of primary solids and initial roughing of the high BOD waste loads and final polishing treatment of the column effluents for removal of remaining organics and color. Anaerobic regeneration was determined to be capable of restoring carbon adsorption capacity to 20.5 to 33.2 kg total COD/day/100 kg carbon. Analyses of heavy metals in the raw wastewater showed them to be below 1.0 mg/ℓ.

TABLE 30. EXPERIMENTAL RESULTS ON THE OCTANOL PLANT WASTE TREATMENT BY VARIOUS PROCESSES

			Effluent		Removal			Operational conditions observed in aeration tank		
Process	BOD mg/ℓ	COD mg/ℓ	BOD mg/ℓ	COD mg/ℓ	BOD percent	COD percent	DT hrs	Loading kg/m^3/day	MLSS mg/ℓ	SVI
Usual activated sludge process (N & P added)	340	440	10	87	97	80	12	0.7	2,870	172
Usual activated sludge process (N, P, Mg, Ca, Fe added	340	440	8	87	98	80	8.0	1.0	2,500	96
	430	544	16	99	96	82	13	0.8	--	--
FAS process	430	544	26	115	94	79	9.5	1.1	--	--
Two stage treatment Primary,	1,260	1,420	19	149	99	90	24	1.3	--	--
FAS process	1,260	1,420	384	504	70	65	10	3.0	--	--
Secondary, Activated sludge	(384)	(504)	19	149	99	90	14	0.7*	4,250	174

*Loading was calculated from 1st stage (FAS) effluent


Influent
Effluent
FAS Aeration Tank
Intermediate Settling Tank
Usual Activated Sludge Process

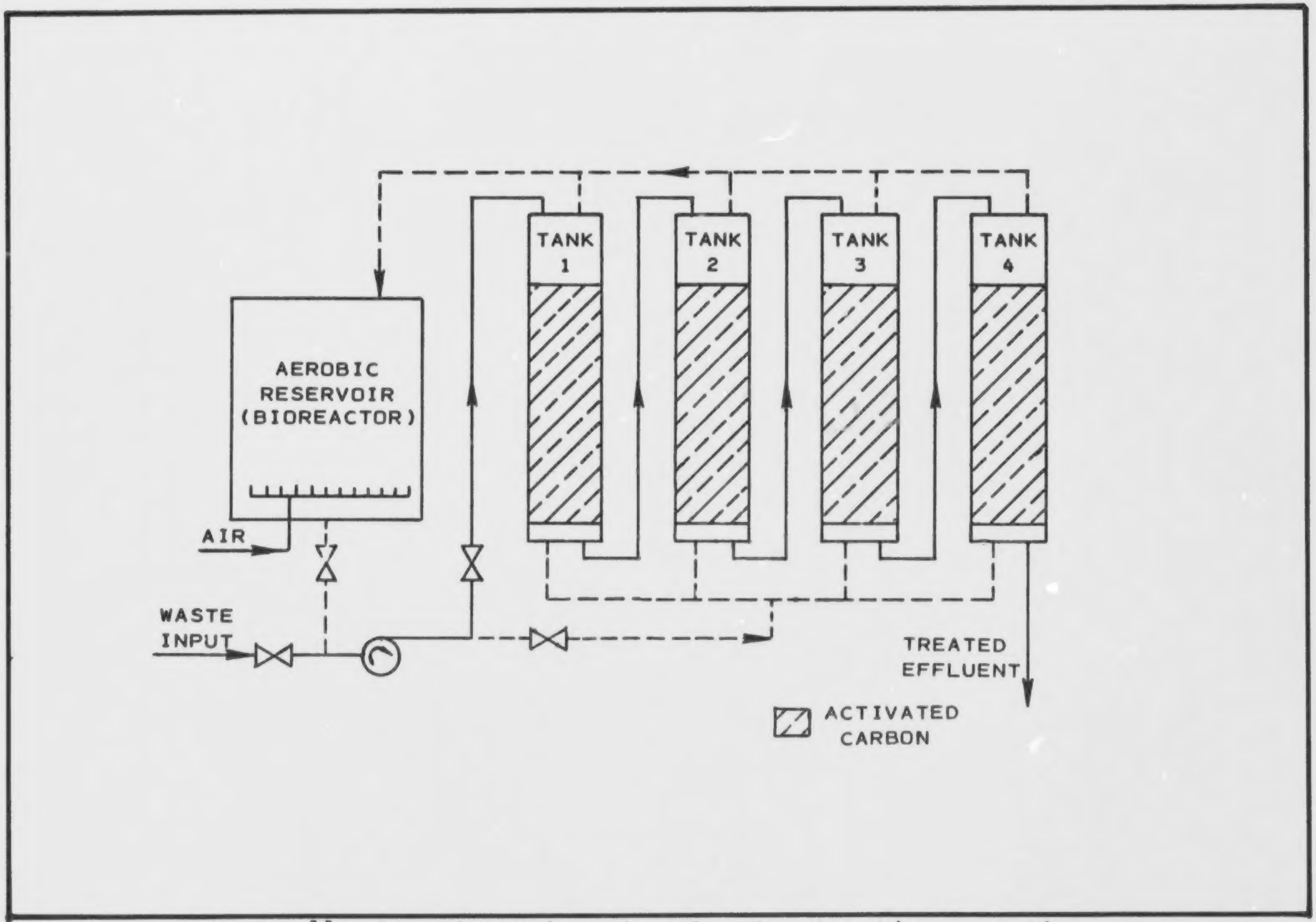

AEROBIC
RESERVOIR
(BIOREACTOR)
AIR
WASTE
INPUT
TANK 1
TANK 2
TANK 3
TANK 4
TREATED
EFFLUENT
ACTIVATED
CARBON

Figure 11. Aerobic activated carbon treatment/regeneration: schematic flow diagram.

An anaerobic regeneration system (134) also functions on an alternating contamination/regeneration treatment cycle. The system operates on a batch sequence basis: for 10 hr, the columns are operating on a contamination cycle, and the filtered waste effluent is discharged; for 14 hr, the columns are back-flushed (regeneration cycle) on a recirculation basis with an aerobic biological culture. During the contamination cycle, liquid flow occurs through each carbon column in series in a downflow mode. During the regeneration cycle, the biological culture flows in a parallel pattern through the columns in an upflow mode. The average results of the operation in terms of COD, TOC, and color are summarized as follows:

Parameter	Raw Influent	Treatment Plant Effluent	Percent Reduction
COD - mg/ℓ	550	280	49.0
TOC - mg/ℓ	220	115	47.8
Color	--	--	99.5

From pilot operations, costs were derived for a proposed 1 MGD plant operating at 50 percent COD and 75 percent TOD removal efficiency. Based upon a 1971 estimate, the following daily power and chemical costs were presented (134):

Treatment	Operating Cost
50% COD Removal	$83/day or 2.2¢/1,000 ℓ
75% COD Removal	$231/day or 6.1¢/1,000 ℓ

The construction cost of a 1-MGD plant is estimated to be:

Treatment	Cost
50% COD Removal	$230,000
75% COD Removal	$550,000

When amortization is fugured into operating costs (capital recovery 20 yr at 8 percent per annum), the costs becomes:

Treatment	Operating Cost
50% COD Removal	\$147/day or 3.8¢/1,000 ℓ
75% COD Removal	\$384/day or 10.1¢/1,000 ℓ

Biological seeding--Biological seeding is sometimes economically feasible for continuous application to large industrial waste treatment systems. Select microbial cultures have also proven useful in serving as start-up seed for full-scale or pilot plants, where specialized wastes are being degraded (164). In addition, bacterial cultures have been applied to batch treatment processes where concentrated wastes have been isolated in spill ponds or equilization tanks. One manufacturer of a freeze-dried, biochemical complex indicates that specialized mutant bacteria can be applied with various nutrients to wastes from pulp mills, chemical plants, refineries, petrochemical complexes, and textile plants. A special culture has also been developed that can remove cyanide toxins from coking and chemical plant wastewaters. Data on one group of freeze-dried bacterial cultures, called Phenobac, are presented below:

Oil Refinery Waste

Treatment System
  Type: Biological Filter/Activated Sludge
  Aeration Time: 12 hr
  Sedimentation Time: 4 hr
  Sludge Return: 25% of influent flow

Treatment Schedule
1) Neutralize influent pH with NH_4OH
2) Adjust influent C/N ratio to 10:1 with diammonium phosphate
3) Add PHENOBAC

		Effluent	
Parameter	Influent	Before PHENOBAC	After PHENOBAC
Flow, m^3/day	1,500.0	1,500.0	1,500.0
BOD_5, mg/ℓ	520.0	95.0	11.0
COD, mg/ℓ	730.0	110.0	75.5

		Effluent	
Parameter	Influent	Before PHENOBAC	After PHENOBAC
Total Solids, mg/ℓ	536.0	229.0	96.5
Suspended Solids, mg/ℓ	235.0	34.0	8.5
Dissolved Solids, mg/ℓ	301.0	195.0	88.0
Oil, mg/ℓ	205.3	20.9	1.5
Phenol, mg/ℓ	86.4	15.7	4.0
Dissolved Oxygen, mg/ℓ	0.2	3.5	4.0
pH	5.7	6.9	7.2

Organic Chemical Plant

Treatment System
Type: Activated Sludge
Aeration Time: 10 hr
Sedimentation Time: 4 hr
Sludge Return: 33% of influent flow

Treatment Schedule
1) Add diammonium phosphate to reduce influent C/N ratio to 10:1
2) Add PHENOBAC

		Effluent	
Parameter	Influent	Before PHENOBAC	After PHENOBAC
Flow, MGD	1.5	1.5	1.5
BOD$_5$, mg/ℓ	1,200.0	335.0	16.0
COD, mg/ℓ	1,815.0	360.0	215.0
Total Solids, mg/ℓ	1,210.0	522.0	188.0
Suspended Solids, mg/ℓ	260.0	50.0	13.0
Dissolved Solids, mg/ℓ	950.0	472.0	0.0
Cyanide, mg/ℓ	18.0	10.0	0.0
Acrylonitrile, mg/ℓ	52.0	18.5	0.0
2-Ethylhexanol, mg/ℓ	225.0	100.0	0.8
Dissolved Oxygen, mg/ℓ	0.2	0.7	4.4
pH	7.5	7.3	7.0

Kraft Mill Waste

Treatment System
Type: Oxidation Lagoons
Installed HP: 1,800
Aeration Time: 24 hr
Sedimentation Time: 8 days

Treatment Schedule
1) Reduce influent pH to 7.5 with waste H_2SO_4
2) Preaerate lagoon entrance channel with 150 HP aerator
3) Add 3 lbs N/100 lbs BOD to reduce influent C/N ratio to 10:1
4) Add PHENOBAC/POLYBAC

		Effluent	
Parameter	**Influent**	**Before PHENOBAC**	**After PHENOBAC**
Flow, MGD	30.0	30.0	30.0
BOD_5, mg/ℓ	300.0	84.0	42.0
Total Solids, mg/ℓ	1,945.0	425.0	358.0
Suspended Solids, mg/ℓ	355.0	135.0	12.0
Dissolved Solids, mg/ℓ	1,590.0	290.0	346.0
Total Alkalinity, mg/ℓ	322.0	125.0	19.0
Color	448.0	420.0	17.0
Dissolved Oxygen, mg/ℓ	0.5	0.1	3.5
pH	9.0	7.5	7.3

Steel Mill Coking Wastes

Treatment System
Type: Trickling Filter/Oxidation Lagoons
Aeration Time: 10 hr
Sedimentation Time: 4 hr

Treatment Schedule
1) Adjust influent pH to 7.1-7.2 with H_3PO_4
2) Add PHENOBAC

		Effluent	
Parameter	**Influent**	**Before PHENOBAC**	**After PHENOBAC**
Flow, MGD	2.0	2.0	2.0
BOD_5, mg/ℓ	685.0	400.0	20.0
COD, mg/ℓ	1,175.0	825.0	138.0
Total Solids, mg/ℓ	680.0	295.0	120.0
Suspended Solids, mg/ℓ	235.0	100.0	13.0
Dissolved Solids, mg/ℓ	445.0	195.0	107.0
Phenol, mg/ℓ	880.0	46.2	0.1
Cyanide, mg/ℓ	25.0	4.4	0.0
NH_3-N, mg/ℓ	3,000.0	178.0	1.3
pH	10.1	9.2	7.1

Textile Plants

Treatment System
  Type: Activated Sludge
  Aeration Time: 10 hr
  Sedimentation Time: 4 hr
  Sludge Return: 33% of influent flow

Treatment Schedule
1) Add diammonium phosphate to yield influent C/N ratio of 10:1
2) Add PHENOBAC

Parameter	Influent	Effluent Before PHENOBAC	Effluent After PHENOBAC
Flow, MGD	2.0	2.0	2.0
BOD_5, mg/ℓ	870.0	314.0	12.0
COD, mg/ℓ	976.0	422.0	325.0
Total Solids, mg/ℓ	1,400.0	835.0	442.0
Suspended Solids, mg/ℓ	850.0	122.0	15.0
Dissolved Solids, mg/ℓ	550.0	713.0	427.0
Oil, mg/ℓ	36.0	21.0	0.5
Mixed Aliphatic Acids, mg/ℓ	112.0	95.3	2.6
Dissolved Oxygen, mg/ℓ	0.0	2.0	3.8
pH	7.1	6.1	7.2

Phenol Waste

Treatment System
  Type: Activated Sludge
  Aeration Time: 10 hr
  Sedimentation Time: 4 hr
  Sludge Return: 25% of influent flow

Treatment Schedule
1) Neutralize influent with NH_4OH to pH 7.0-7.2
2) Adjust influent C/N ratio to 10:1 with diammonium phosphate
3) Add PHENOBAC

Parameter	Influent	Effluent Before PHENOBAC	Effluent After PHENOBAC
Flow, m^3/day	1,500.0	1,500.0	1,500.0
BOD_5, mg/ℓ	850.0	320.0	9.7
COD, mg/ℓ	1,224.0	432.5	25.8
Total Solids, mg/ℓ	1,200.0	535.0	336.5

Parameter	Influent	Effluent Before PHENOBAC	Effluent After PHENOBAC
Suspended Solids, mg/ℓ	145.0	55.0	22.0
Dissolved Solids, mg/ℓ	1,095.0	480.0	314.0
Phenol, mg/ℓ	332.0	107.0	0.02
NH_3-N, mg/ℓ	0.0	9.6	1.1
Dissolved Oxygen, mg/ℓ	0.0	2.5	3.8
pH	5.4	7.1	7.0

Laboratory experiments indicate that these bacteria cultures are also effective in degrading halophenols, aliphatic and aryl amines and aryl halides. The manufacturers indicate that Phenobac effectiveness will be greatly diminished unless the wastewater treatment system meets the following conditions:

Parameter	Optimum	Minimum	Maximum
Influent pH	7.0	4.5	9.5
Dissolved oxygen, mg/ℓ	3.0+	2.0	None
C/N/P	100/10/1	None	200/10/1
Temperature, °C	30	10	40
Toxic metals, mg/ℓ (e.g., hex. chromium)	<1	None	≤2

Such limitations restrict the types of waste streams that may be subject to innovative biological seeding. Furthermore, continuous seeding must be conducted to maintain a viable degrading population where there are adverse environmental conditions, other microbial predators, or excessive washout. The cost of continuous additions of large volumes under such circumstances may be noncompetitive with alternative treatment methods.

Powdered activated carbon treatment (PACT)--The results of several full-scale tests of powdered activated-carbon addition to a variety of chemical plant effluents is described by A. D. Adams (1). According to Adams, the addition of powdered carbon to waste streams prior to their introduction into aerated or activated-sludge systems:

- Improves BOD and COD removals despite hydraulic and organic overloadings
- Aids solids settling, decreases effluent solids, and yields thicker sludge
- Adsorbs dyes and toxic components that are either not treated biologically or are poisonous to the biological system

- Reduces aerator and effluent foam by adsorption of detergents

- Prevents sludge bulking over broader F/M ranges

- Effectively increases plant capacity at little or no additional capital investment

- Gives more uniform plant operation and effluent quality, especially during periods of widely varying organic or hydraulic loads.

Test results with activated carbon at an ICI American facility manufacturing polyols and derivatives are cited. By adding sufficient powdered activated carbon to maintain a level of 1,000 ppm in the 568-m^3/day (150,050 gal/day) system, COD and BOD removals were increased 25 and 20 percent, respectively. In another test at a municipal waste treatment plant treating 70-percent industrial flow from a textile plant, activated carbon in the waste at 900 ppm effectively stabilized the variability of BOD removals.

Adams further notes that there are presently no full-scale wastewater treatment plants that regenerate spent powdered carbon on a continuous basis, although several have been suggested. Experience showed that typical treatment costs for activated-carbon addition can vary from 0.4 to 1.8 cents/1,000 ℓ. Savings may also be incurred since fewer defoamers, coagulants, and coagulant aids are needed. Sludge conditions may also be improved by the presence of the carbon.

Pilot testing of the DuPont PACT process at DuPont Chambers Works organic chemicals plant is reported by Flynn (45). Research indicated that removals of COD and TOC due to carbon alone can be computed; such removals are likely to increase with sludge age. Results of experiments with five continuous-flow laboratory PACT units treating a variety of high, medium, and low sludge ages and temperatures are shown in Table 31. Additional laboratory studies (80) have indicated that the activated carbon effectiveness in activated sludge systems is primarily due to surface concentrating effects in systems of dilute waste concentrations. The carbon can also adsorb toxins, thereby reducing the toxin concentration to a level where it is not inhibiting and may be slowly degraded.

Cooling tower biooxidation--Cooling towers can also supplement conventional biological conversion. The enhanced surface area of the tower and resultant increase in dissolved oxygen in the cascading waste stream promote biological growth within cooling towers. One cooling tower system reported in the literature (50) removes 1,727 kg (3,808 lb) of BOD/day and reduces

TABLE 31. CARBON ADDITION TO ACTIVATED SLUDGE - DUPONT PACT PROCESS (45)

	Summary of Results							
Temperature (^oC)	31	31	25	21	20	13	7	7
Residence Time (days)	0.203	0.184	0.254	0.157	0.169	0.188	0.191	0.206
Sludge Age (days)	14.1	5.5	13.4	8.4	8.7	14.7	11.2	3.9
Feed Carbon Concentrate (mg/ℓ)	158.4	148.3	152.1	149.8	159	147.8	152	166
Feed BOD (mg/ℓ)	151	151	153	147	145	153	148	154
Effluent BOD (mg/ℓ)	2.7	6.8	2.6	2.8	2.7	4.5	8.8	34.5
Mixed Liquor Suspended Solids	14,297	6,518	10,667	11,223	11,145	15,242	11,975	4,380
Biological TSS (mg/ℓ)	3,311	2,082	2,630	3,190	2,977	3,657	3,004	1,221
Loading (mg BOD/mg Biomass-d)	0.220	0.375	0.224	0.287	0.282	0.216	0.244	0.477

the phenol concentration from 12 to 0.09 mg/ℓ. A similar system was reported to reduce the phenolic concentration from 3 to 0.06 mg/ℓ. It was also noted that periodic blowdowns and system cleaning due to biological sloughing result in high BOD slugs.

Biooxidation of reuse waters in a petroleum refinery has resulted in considerable water quality improvement and subsequent reduction in water demand (112). However, care should be taken to determine those organic compounds that are converted in biological processes and those that are stripped into the atmosphere by the forced or induced air draft. This is especially true for the volatile, less soluble compounds and may result in secondary air pollution problems. The rate of corrosion of cooling tower structures is not accelerated greatly because of the accumulation of biological slimes and biooxidation processes.

Innovative Operational Methods--

Automation/optimization--Understanding of the mechanisms and kinetics of biological waste treatment processes is continually increasing. As the interrelationships of various treatment components are understood, treatment plant designers and operators are attempting to improve processes. Automation and feedback process control are being utilized more and more. Key waste and operational parameters are being identified and characterized. Many of these parameters may be continuously measured or determined from automatic composite sampling. Signals from continuous monitors or data from samples may be automatically used to compute independent control variables or used to directly control operational processes. Such systems are known as optimal feedback control systems and rely heavily upon continuous or semicontinuous sampling and automated process control. The objectives of control actions are to maintain the desired rate of bioconversion in the bioreactor although other parameters, such as suspended solids in the final effluents or cost of chemical additions, may also be considered.

In waste treatment plants where computerized process optimization is practiced, it is imperative that a process model be defined in the control program. An understanding of the kinetics of biological and chemical reactions is especially important. A discussion of the development of modern optimal feedback control models and their required inputs is presented by Fan et al. (43).

Where real-world process monitoring inputs are not utilized, process models may still be used in computer simulation studies to determine optimum operational modes. Alternative models may also be compared for selecting better operational methods (32).

The application of treatment optimization through automation at a Dow Chemical Company petrochemical plant was tested by Zeitoun et al. (169). A summary of the system is presented below:

> Instrumentation and control of an industrial, activated-sludge pilot plant was accomplished by development of systems controlling the critical parameters of the process to achieve reliable, high quality effluent. Optimization techniques based on the steady-state and transient models of the activated sludge process were used to determine the minimum volume of the aeration basin required for a specified effluent quality and to predict the transient conditions as a result of step changes in loading.
>
> A pH control system stopped plant operations for the duration of the upset, automatically restoring it when the feed pH returned within operating limits. An automated sampling system, sampling feed and homogenized mixed liquor, monitored the total carbon in both samples. Nutrients (nitrogen and phosphorus) were added in proportion to the total carbon in the feed, thus maintaining low residual nutrients in the effluent. The sludge recycle flow rate was controlled by a food to microorganisms (F/M) signal, measured as the ratio of total carbon in the feed to that in the mixed liquor. Response time of the F/M control system to a step increase in feed concentration was reduced by 50 to 70 percent, as compared to the uncontrolled system, depending on the amount of excess sludge available for recycle. Chemical flocculants were added in proportion to the turbidity of the biosettler overflow, removing 85 to 98 percent of the suspended solids. Toxic or inhibitory effects of the feed were measured by a biological inhibitor detector, an instrument that measures the oxygen uptake of standard solutions before and after exposure of a bacteria sample to a feed sample and calculates an activity ratio, that had an automated cycle of 60 min. The use of the instrument as an upstream sensing device was demonstrated as toxic substances were added to the feed (169).

Cost evaluations for such systems can vary greatly depending upon the degree of automation and sophistication of the monitoring and data analyzing hardware. In addition, most full-scale automation has been conducted only at a pilot level and it would be difficult to make cost estimates for a full-scale plant. However, this technology will be used more and more in the future to meet stringent discharge standards and avoid fluctuations in discharge loadings. Plant owners and operators will be better able to evaluate the benefits that such systems may provide for their particular plants.

MICROBIAL ASSIMILATION OF ORGANIC WASTES

There is relatively little information in the literature describing microorganisms capable of metabolizing recalcitrant organic materials. Most studies have considered mono-cultures and idealized carbonaceous substrates applied under carefully controlled laboratory conditions. Such experiments are not affected by the same complex biochemical, ecological, and successional relationships typical of anaerobic lagoons, sludges, aeration basins, and other treatment plant environments. Moreover, analyses of industrial treatment plant waste streams for microbial populations do little to predict the efficiency of biodegradation. Gross observations of these populations can be helpful in determining which orders of bacteria, actinomycetes, fungi, yeast, or protozoa will predominate with known plant environments and waste characteristics. Such information provides a foundation for future studies of complex population interactions and has proved useful in selecting proper microbial seeds for either starting or accelerating biological treatment of certain organic wastes.

The results of a literature survey of microorganisms that can assimilate recalcitrant organic materials are shown in Table 32. Appendix A presents a bibliography of material related to the microbial assimilation of organic wastes. Extensive growth tests conducted with various bacteria, fungi, yeast, and other microbes on saturated hydrocarbons, aliphatics, aromatics, and hydrocarbon mixtures show Pseudomonas to be the most capable. Early studies of microorganisms that can assimilate paraffin wax are reported by ZoBell (170). His work shows that soils, sediments, and water are the major reservoirs of hydrocarbon-degrading populations. The ability to metabolize hydrocarbon substrates appears to be widespread; more than 200 species (28 bacterial, 30 filamentous fungal, and 12 yeast genera) have been shown to utilize hydrocarbons (31).

Organic chemicals and synthetics have also been demonstrated to be amenable to biological degradation. Bayley and Wigmore (13) have studied the growth of mutant strains of Pseudomonas putida on phenol and cresols, and fungi have been observed growing in jet fuels (128) and toluene (115). Phenylmercuric acetate has been shown to support growth of Pseudomonas, Arthrobacter, Citrobacter, Vibrio, Flavobacterium, and Enterobacter. ZoBell (171) reported the growth of actinomyces and bacteria on various rubber compounds including polymerized olefinic hydrocarbons, raw or crepe rubber, and hevea latex. Detergent compounds, particularly linear alkyl benzyl sulfonates, are readily degraded in waste treatment plants. Two bacteria genuses are responsible for this decomposition: Nocardia and Pseudomonas (108).

TABLE 32. LIST OF MICROORGANISMS REPORTED BY VARIOUS AUTHORS TO ASSIMILATE RECALCITRANT ORGANIC MATERIALS

Reference (See Appendix A)	Waste Description	Microorganisms
Blevens and Perry (1972)	methylamine	Pseudomonas sp. gram-negative diplococcus
	propane	Mycobacterium vaccae (JOB5) album strains 7E4 and 7E1B1W M. rhodochrous strains OFS, A78 and 7E1C
Bavley and Wigmore (1973)	phenol cresols	Mutant strains of Pseudomonas putida (strain U)
Markovetz and Kallio (1964)	hydrocarbons of chain length C_{10}-C_{18}	Rhodotorula, Trichosporn, Candida lipolytica and Candida pulcherrima
Miller et al. (1964)	chain length C_{12}-C_{18}	Candida intermedia
Scheda and Bos (1966)	n-hexadecane n-decane kerosene	Rhodotorula sp., Pichia, Debaryomyces, Candida, Torulopsis
Otsuka et al. (1966)	kerosene hydrocarbons of chain length C_{10}-C_{16}	Candida tropicalis C. tropicalis, C. cloacae
Lowery et al. (1968)	n-alkanes	Candida, Rodotorula, Debaryomyees
Iida and Iizuka (1970)	1-decene	Candida rugosa
Barua et al. (1970)	paraffins	Trichosporon pullulans
Prince (1961)	jet fuels	Cladosporium, Hormodendrum
Kester (1961)	n-tridecane	Aspergillus aliaceus, Cephalosporium roseum, Colletotrichum altramentarium, Acremonium patronii, Fusarium balbigenum, and Monila bonordenii
Krause and Lange (1965)	n-alkanes C_{11}, C_{20}, C_{22}, C_{23}, C_{28}, C_{32}	three species of Fusarium
Nyns et al. (1968)	hydrocarbons, toluene	Fusarium, Penicillium, Paecilomyces, Chloridium, Oidiodendron, and Scolecobasidium

TABLE 32 (continued)

Author	Waste Description	Microorganisms
Lowery et al. (1968)	hydrocarbons	Aspergillus, Cephalosporium, Dematium, Epicoccum, Fusarium, Gliocladium, Graphium, Mucor, Paecilomyces, Penicillum, and Trichoderma
Stone et al. (1942)	various oils	pseudomonads
Webley (1954)	n-dodecane, n-tetradecane n-hexadecane n-octadecane	Norcadia opaca
Treccani et al. (1955)	numerous compounds from C_3- C_{28} C_3-C_{12}	norcardia, mycobacterium achromobacter
Walker and Colwell (1974)	petroleum	mercury-resistant strains of Pseudomonas, Arthrobacter, Flavobacterium Vibrio, Citrobacter.
Nelson et al. (1973)	phenylmercuric acetate	Pseudomonas, Arthrobacter, Citrobacter, Vibrio, Flavobacterium, Enterobacter
Makula and Finnerty (1972)	tetradecane pentadecane hexadecane	Micrococcus cerificans
Atlas and Bartha (1972)	crude oil	Brevibacterium sp., Flavobacterium sp.
Walker and Colwell (1974)	petroleum	Cladosporium resinae
Zajic and Knettig (1972)	kerosene	Corynebacterium hydrocarboclastus
Scott and Hancher (unpublished)	phenol	Pseudomonas Putida
LaRock and Severance	hydrocarbon mixture	Brevibacterium
Zobell (1969)	kerosene jet fuel paraffin wax	Aspergillus, Botrytis, Candida, Cladosproium, Debaromyces, Endomyces, Fusarium, Hansenula, Monilia, Penicillium, Actinomyces, Micromonospora, Nocardia, Proactinomyces, and Streptomyces
Novelli and Zobell (1944)	aliphatic hydrocarbons	Desulfovibrio

TABLE 32 (continued)

Author	Waste Description	Microorganisms
Mulkins-Phillips and Stewart (1974)	crude oils	Norcardia, Pseudomonas, Flavobacter, Vibrio, and Achromobacter
ZoBell (1950)	caoutchouc (polymerized olefinic hydrocarbons)	Actinomyces alba, A. chromogenes, A. elastica, A. fuscus, Bacillus mesentericus, Mycobacterium lacticola, M. rubrum, and Pseudomonas fluorescens
	raw or crepe rubber	Serratia marcescens
	plantation rubber/ hevea latex	Aspergillus and Penicillium Alcaligenes denieri, Bacillus pandora, Gaffkya verneti, Micrococcus chersonesia, M. eatoni, M. epimetheus, M. ridleyi, and Forulae heaveae
Kaufman and Plimmer (1972)	aliphatic acids	Norcardia sp.
Mitchell	w-phenoxyalkanoates	Norcardia coeliaca
	malathion	Trichoderma viride
Mitchell (1974)	pesticides	Pseudomonas, Bacillus, Flavobacterium, and Achromobacter/Norcardia, Aspergillus
	detergents	Nocardia, Pseudomonas
Cooper (1963)	rendering plant wastes (anaerobic)	Thiopedia rosea
	petroleum refinery waste (anaerobic)	Chromatium sp.
Taber (1976)	pulp mill wastes	Azotobacter, Klebsiella, Rhodotorula, Hansenula, and Pichia
Callely et al. (1976)	industrial effluents	Achromobacter, Alcaligenes, Comomonas, Flavobacterium, Pseudomonas, Thiobacillus and Zoogloea
Cooney and Walker (1973) Ahearn	hydrocarbons	Cladosporium resinae
Gibson and Yeh (1973) Ahearn	benzene toluene ethylbenzene p-Fluorotoluene p-Chlorotoluene p-Bromotoluene	Pseudomonas putida
	Naphthalene	Pseudomonas sp.
	biphenyl	Beijerinckia sp.

TABLE 32 (continued)

Author	Waste Description	Microorganisms
Perry and Cerniglia (1973) Ahearn	petroleum	Cunninghamella elegans Penicillium zonatum Aspergillus versicolor Cephalosporium acremonium Penicillium ochro-chlorens
Finnerty et al. (1973) Ahearn	hexadecane	Acinetobacter sp.
Soli (1973) Ahearn	hydrocarbons	Arthrobacter sp., Mycobacterium paraffinicum
Guire (1973) Ahearn	hexadecane	Candida petrophilum Pseudomonas aeruginosa
Hollackov et al. (1976)	weak ammoniacal liquors (coal coking)	Bacillus, Stapholoccus (not aureus), Pseudomonas, Citrobacter, Proteus and E. Coli
Shelton and Hunter (1975)	oils (in anaerobic sediments)	Desulfovibrio
Sivela and Tuovinen	methyl mercaptan dimethyl sulfide dimethyl disulfide	thiobacilli

TABLE 33. MICROORGANISMS KNOWN TO METABOLIZE ORGANOCHLORINE PESTICIDES (152)

Reference (See Appendix A)	Pesticides	Microorganism
		Bacteria
Patil et al. (1970)	Endrin, DDT	Arthrobacter
Patil et al. (1970)	Endrin, DDT	Bacillus
McRae et al. (1969)	Lindane	Clostridium
Mendel and Walton, (1966)	DDT	Escherichia
Focht, (1972)	DDT	Hydrogenomonas
Wedemeyer, (1966)	DDT	Klebsiella
Patil et al. (1970)	Endrin, Aldrin, DDT	Micrococcus
Barker et al. (1965)	DDT	Proteus
Patil et al. (1970)	Endrin, Aldrin, DDT	Pseudomonas spp.
Bourquin et al. (1971)	Heptachlor	Pseudomonas spp.
Matsumura et al. (1968)	Dieldrin	Pseudomonas
Patil et al. (1972)	Dieldrin, Aldrin Endrin, DDT	Unidentified
Lichtenstein and Schulz, (1959)	Lindane, Aldrin	Unidentified
		Actinomycetes
Chacko et al. (1966)	DDT, PCNB	Nocardia
Chacko et al. (1966)	PCNB	Streptomyces
		Fungi
Chacko et al. (1966)	PCNB	Aspergillus
Focht, (1972)	DDT	Fusarium
Anderson et al. (1970)	Dieldrin	Mucor
Bixby et al. (1971)	Dieldrin	Trichoderma
		Yeast
Kallerman and Andrews, (1968)	DDT	Saccharomyces
		Algae
Sweeney, (1968)	Lindane	Chlamydomonas
Patil et al. (1972)	Aldrin	Chlorella and Dunaliella

Bourquin (20) has reported extensively on microorganims, chiefly soil and aquatic, which can partially degrade chlorinated hydrocarbon pesticides in various environments (Table 33). Beneckea and Caulobacter have been predominately represented by marine or estuarine genera. It should be noted that microbial degradation, which is probably the major natural mode of pesticide reduction in the environment, is most often incomplete and results in metabolites which may or may not exhibit toxic or mutagenic characteristics. The degradation of DDT to DDE or DDD, for example, results in products which can be bioaccumulated and create lasting negative impacts.

Microbes growing on organics leaving pulp and paper mills are nitrogen-fixing Azotobacter and Klebsiella (153) and the yeasts Rhodotorula, Hansenula, and Pichia. It is indicated that yeasts can remove resins from kraft mill effluents. Holladay et al. (64) report Bacillus, Stapholococcus, Pseudomonas, Citrobacter, Proteus, and *Escherichia coli* in association with weak ammoniacal liquors from the coal-coking process.

SECTION IV

SITE STUDIES

INTRODUCTION

In compiling and reviewing information for Section III, the project staff became aware of various biodegradation techniques being employed to treat problematic and/or large quantities of industrial organic materials. This fourth section includes detailed site studies on four biological treatment systems handling industrial organic materials. Each study contains information on:

- Waste identification
- Treatment system construction and design
- Operations (parameters measured and methods)
- Treatment efficiency
- Economics.

The site selection process took place in four steps, outlined below and discussed in the following paragraphs.

Step 1: Review literature and contact various sources for study site suggestions and information

Step 2: Establish site selection criteria

Step 3: Use site selection criteria to determine applicability of biological process(es) to this study

Step 4: Present and finalize selected sites with the EPA.

To determine the biodegradation techniques used for treating industrial organic materials in 1977, SCS Engineers chose to incorporate an initial literature search followed by personal contact with individuals familiar with current biological treatment techniques. These contacts included:

- State, provincial, and national governing bodies in both the United States and Canada

- Equipment and hardware manufacturers

- Engineering consulting and design firms

- Private industry
- Institutes and societies
- Universities and colleges.

This step one search identified 19 potential study sites.

Site selection criteria were developed to assist both the EPA and SCS Engineers in determining the site applicable to the goals of the project. The site selection criteria were:

- Cooperation and applicability to project goals
- Geographic location
- Variety of organic materials treated
- Availability of system data
  - Influent, effluent, and sludge waste streams
  - Design
  - Operation
  - Costs: capital, operational, and maintenance.

Four sites which best satisfied these criteria were chosen as representative of biological treatment techniques for organic materials. These sites are described in detail in the following pages.

GULF COAST WASTE DISPOSAL AUTHORITY (GCWDA)
40-ACRE INDUSTRIAL WASTE TREATMENT FACILITY
TEXAS CITY, TEXAS

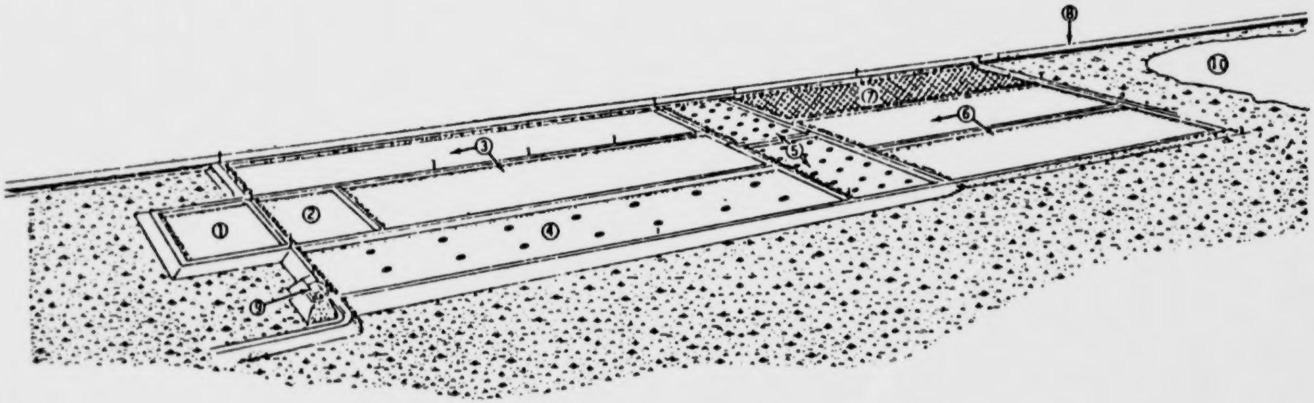
INTRODUCTION

The Gulf Coast Waste Disposal Authority (GCWDA) 40-Acre facility consists of a series of lagoons biologically treating raw and primary treated petrochemical and industrial wastewaters. The waste streams were chosen by GCWDA for their amenability to biological treatment and their ability to supply required nutrients for biological degradation. The lagoons have a surface area of 50.6 ha (125-ac) and treat a flow of 50,000 to 57,000 m^3/day (13 to 15 MGD). Maximum possible retention time in the system is 21 days. The biological lagoon series is as follows: anaerobic, limited aerobic, aerobic, and faculative lagoon wastewater biodegradation. Figure 12 shows the arrangement of the lagoons:

Various problems are encountered in the conventional biological treatment of industrial and especially petrochemical wastewaters. Difficulties include (65):

- Elevated temperatures which are detrimental to microorganism flocculation and separation
- Surfactants causing foaming problems
- Synthetic organic constituents inhibitory to nitrifiers, protozoa, and flocculating organisms
- Varying qualities and quantities of organic wastes discharged from a large petrochemical complex resulting in nonequilibrium conditions.

To help combat these potential problems, the designers of the 40-Acre facility proposed a system with large volume and long treatment retention time. The large volume of this lagoon system allows absorption of major waste quality changes without significantly altering the bulk quality of the system contents. The large surface area permits cooling to ambient temperatures. Anaerobic treatment helps to stabilize problem materials such as surfactants and reduce oxygen demand before aerobic treatment. In addition, the open lagoon system provides an environment in which photosynthetic bacteria and algae may proliferate. Near the lagoon surface, aerobic bacteria may utilize surface entrained



1 Emergency Holding Basin
2 Equalization Basin
3 Anaerobic Lagoons
4 Limited Aeration Basin
5 Aerated Stabilization Basins
6 Facultative Basins
7 Undeveloped Area for Future Facultative Basins
8 Hurricane Levee Pump Discharge Canal
9 Office and Laboratory Building
10 Swan Lake

Figure 12. GCWDA 40-Acre facility layout.

and photosythetically produced oxygen to aerobically stabilize organic wastes and oxidize inorganics such as sulfides.

History

The GCWDA is a public authority formed by the Texas State Legislature in September 1969 to participate in industrial waste treatment. On May 29, 1971, the Texas Water Quality Board (TWQB) issued a Waste Control Order to the GCWDA to build and operate a waste treatment facility at Texas City, Texas. Design engineering was completed in 1971, construction began in early 1972, and initial operation commenced in 1974.

There has been only one major system modification at the facility since the initial construction. In February 1976, the addition of 14 aerators converted the southernmost anaerobic lagoon to a limited aeration lagoon.

Location

The 40-Acre facility is located approximately 56 km (35 mi) southeast of Houston and 1.6 km (1 mi) south of Texas City, which is 0.8 km (1/2 mi) from Galveston Bay and 0.4 km (1/4 mi) from Swan Lake. Figure 13 shows the location of the facility, which is located on the unrelieved flat Gulf Coast plain. The area immediately surrounding the facility is a combination of tideland and marshland. The soil is comprised of silty clay materials.

Regional Characteristics

Petrochemical-related industries are numerous in the Houston-Texas City area. This region contributes 30 percent of the total United States petrochemical output (51). Economic reasons for growth of the industry in this area include the availability of sea transport and the location of 75 percent of United States petroleum reserves within easy reach. Additional factors include an abundance of water needed to meet industrial demand and ease of pipeline construction on and under the flat terrain.

The climate is humid and subtropical. Temperatures are moderated by winds from the Gulf of Mexico, producing mild winters. The location is, therefore, ideal for a large lagoon treatment system. Rainfall is abundant, averaging 122 cm (48-in) per year, and dry periods are rare (159). Evapotranspiration averages between 107 and 114 cm (42 and 44 in) annually (150).

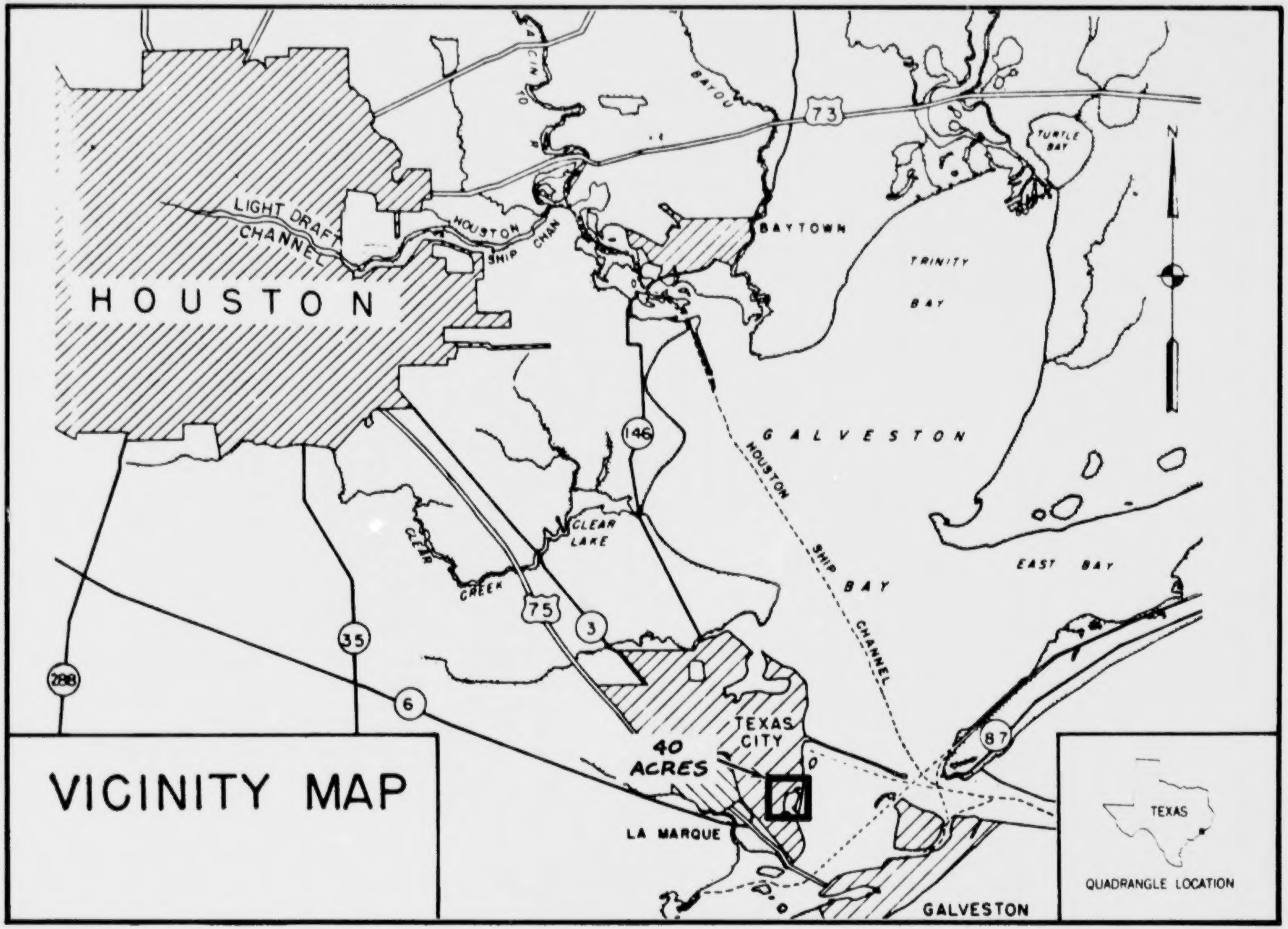

VICINITY MAP
HOUSTON
LIGHT DRAFT CHANNEL
HOUSTON SHIP CHAN
SAN JACINTO R
BAYOU
73
BAYTOWN
TURTLE BAY
TRINITY BAY
N
GALVESTON
HOUSTON SHIP BAY CHANNEL
EAST BAY
146
CLEAR LAKE
CLEAR CREEK
75
3
35
288
6
40 ACRES
TEXAS CITY
LA MARQUE
87
GALVESTON
TEXAS
QUADRANGLE LOCATION

Figure 13. Location of GCWDA 40-Acre facility.

WASTEWATER IDENTIFICATION

Sources

Three companies currently supply the wastewater influents to the GCWDA 40-Acre treatment facility (Figure 14). The number and types of waste streams and the monitoring data available have varied during the past operation of the facility. Figure 15 summarizes the waste streams that were treated at 40-Acre from January 1975 to March 1977.

Discharger 1--

Discharger 1 generates two major waste streams identified as diluted and concentrated at the Texas City petrochemical plant and provides primary treatment for both. In-plant waste streams which make up Influent A are mixed and physically cleaned of debris at a junction box. Caustic may be added at this point if necessary. Influent A then flows into two parallel center-feed, 27.4 m (90-ft) diameter primary clarifiers. After clarification, the supernatant is pumped 4.8 km (3 mi) to the 40-Acre facility.

Influent B_1 flows into a skimmer unit where flotables are removed. The waste stream is then pumped to an Off Plant Disposal Area (OPDA) maintained by Discharger 1 and located adjacent to the 40-Acre facility (Figure 14). The OPDA consists of long-retention-time (up to one year) facultative lagoons for the stabilization of the high organic content of the wastewater. The effluent from the OPDA (Influent B) is transported to the 40-Acre facility for further treatment.

On October 25, 1976, pumping of Influent B_1 to the OPDA was suspended and instead the wastewater was pumped directly to the 40-Acre facility anaerobic lagoons. Various odoriferous mercaptan compounds were generated in the lagoons. This had not previously occurred in the 40-Acre anaerobic lagoons when influent B was treated. The odors led to the termination of direct pumping of Influent B_1 to 40-Acre and reactivation of the OPDA on March 24, 1977. Scientists from GCWDA and Discharger 1 are currently attempting to identify and isolate the problem compounds.

Characteristics--Following is a description and characterization of the three waste streams from Discharger 1 transported to the 40-Acre facility.

Flow of Influent A averages between 3.4 to 4.2 x 10^4 m^3/day (9 to 11 MGD) with a pH of approximately 9. Temperature fluctuates between 30 and 45°C. Tables 34 and 35 summarize data on Influent A constituent concentrations average loading values,

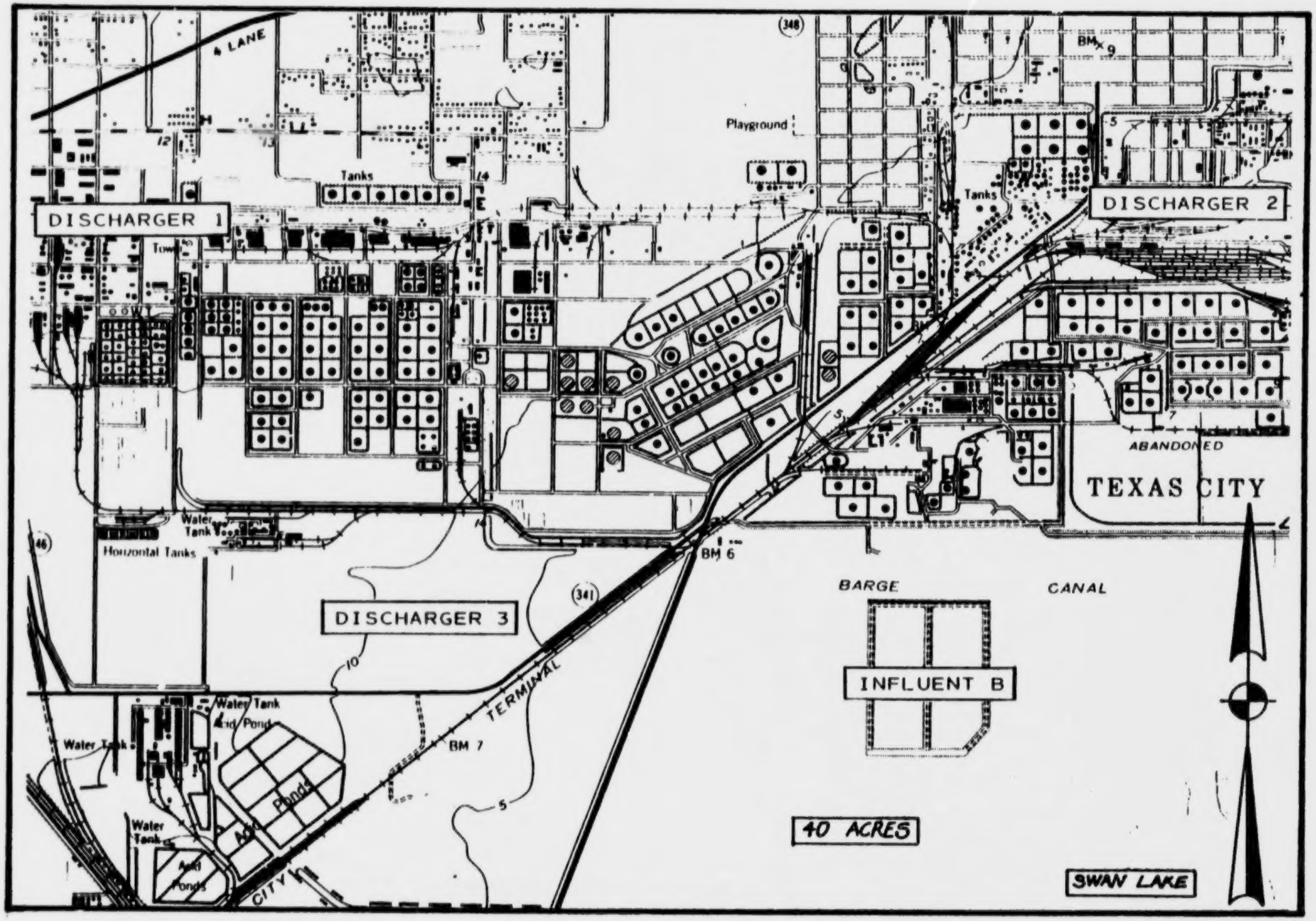

4 LANE
12
13
Tanks
14
DISCHARGER 1
Town
(348)
Playground
BM 9
5
Tanks
DISCHARGER 2
ABANDONED
TEXAS CITY
Water Tank
Horizontal Tanks
(46)
BM 6
(341)
DISCHARGER 3
10
BARGE
CANAL
INFLUENT B
TERMINAL
Water Tank
And Pond
Water Tank
BM 7
Acid Ponds
Water Tank
Acid Ponds
5
CITY
40 ACRES
SWAN LAKE

Figure 14. Location of industries supplying influent to 40-Acre facility.

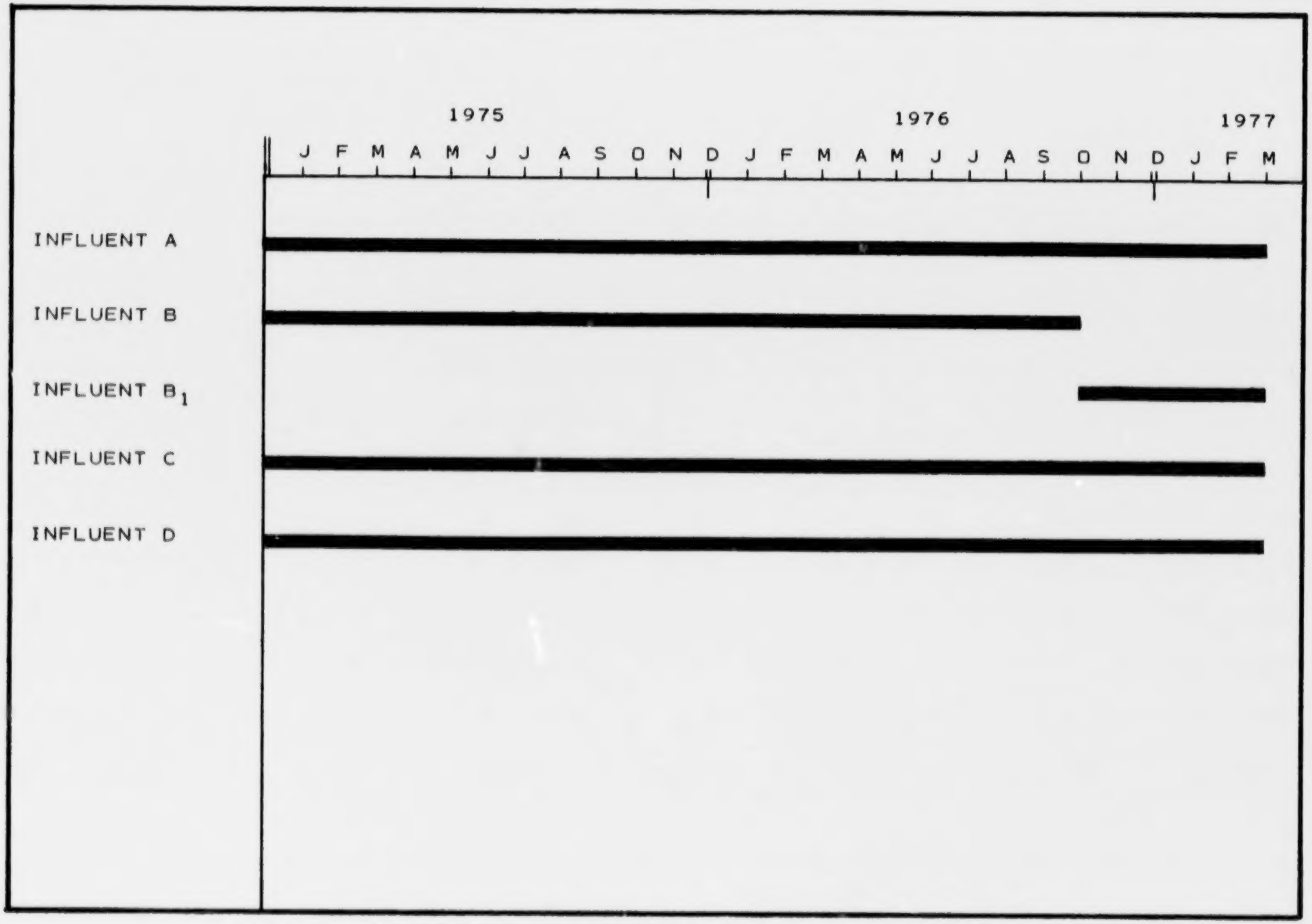


Figure 15. Historical representation of waste streams entering the GCWDA 40-Acre treatment facility.

TABLE 34. CHARACTERIZATION OF INFLUENT A (mg/ℓ)

Parameter	1975		1976		1977*	
	Average	Range	Average	Range	Average	Range
TOC	265	208 - 388	255	205 - 282	316	229 - 367
COD	903	658 -1349	910	766 -1129	1141	795 -1315
BOD	404	283 - 581	467	381 - 609	498	288 - 678
TSS	141	61 - 254	99	56 - 151	164	129 - 198
VSS	60	36 - 90	46	29 - 87	65	50 - 76
TDS	5352	3387 -6869	3687	2553 -4443		
Chloride	2607	1617 -3295				
Sulfide	75.3	54.0 -109.9	81.9	46.4 -118.7	51.7	47.1 -59.3
Phosphorus	15.7	1.55- 36.6	4.12	1.46- 9.31	7.05	4.06 -9.04
Fluoride	2.62	2.47- 2.97	1.01	0.127- 2.84		
TKN	79.8	19.1 -156.2	9.43	2.39- 23.1	26.1	19.1 -33.7

* Average of Jan-Mar 1977

TABLE 35. CHARACTERIZATION OF INFLUENT A LOADING TO THE 40-ACRE FACILITY

Parameter	1975 Average kg/day (lb/day)	1975 Standard Deviation	1975 Total kg/yr	1976 Average kg/day (lb/day)	1976 Standard Deviation	1976 Total kg/yr
TOC	9864 (21746)	2635	3594181	9336 (20582)	934	3406545
COD	33545 (73954)	7185	12209727	33263 (73332)	4704	12473045
BOD	15136 (33369)	3434	5510045	17168 (37849)	3044	6261272
VSS	2223 (4901)	626	808318	1682 (3708)	522	614727
TDS	197727 (435913)	33330	72156000	139318 (307144)	33883	50851136
Chloride	96227 (212144)	16511	35103227			
Sulfide	2795 (6162)	776	1025363	3009 (6634)	1034	1094863
Phosphorus	591 (1303)	454	215772	154 (340)	68	56682
Fluoride	100 (220)	23	36500	36 (80)	27	13364
TKN	2968 (6543)	1910	1089181	336 (741)	231	123727

respectively. The specific volatile organics identified in the waste stream are (74):

- Methanol
- Ethanol
- Isopropanol
- Acetaldehyde
- Acetone
- Methyl ethyl ketone
- Benzene
- Ethylene glycol
- Acetic acid.

Influent B_1 is characterized by a flow of less than 5.7×10^3 m^3/day (1.5 MGD) and a high organic concentration, averaging 20,000 mg/ℓ COD. In addition to the volatile organics present in Influent A, the concentrated waste stream contains (74):

- Propionic acid
- Butyric acid
- Pentanol
- C_5-aldehydes
- C_5-acids
- C_6-alcohols
- Phenol
- Butyl ethers
- Propyl ethers
- Methyl isobutyl ketone
- C_{10}-18 alcohols
- Formate.

Table 36 summarizes the average monthly concentration and loading values for Influent B_1.

Effluent from the OPDA (Influent B) enters the 40-Acre facility at ambient temperature; flows average 3.79×10^3 m^3/day (1.0 MGD). The complex organics of Influent B_1 are oxidized in the OPDA into simpler volatile acids and ketones, acetone, methyl ethyl ketone, and methyl isobutyl ketone. COD values in the effluent average 1,500 mg/ℓ. The increased sulfide concentration in the OPDA effluent is an indicator of sulfate utilization as an inorganic oxygen source. Tables 37 and 38 illustrate yearly concentration and loading values, respectively.

Influent C, from Discharger 2, is characterized by a flow averaging $1.14 \times 10^4 \times 10^4$ m^3/day (3.0 MGD) and a pH of approximately 8. The waste stream has a high organic loading: BOD 9409 and COD 16,318 kg/day (20,743 and 35,975 lb/day). The raw waste stream requires pretreatment to remove potentially disruptive cyanide before transportation to 40-Acres. Tables 39 and 40 show concentration and loading values for Influent C.

Influent D is the result of the collection of water runoff from a phosphate fertilizer manufacturing plant. Although the flow of 6.4×10^2 m^3/day (0.17 MGD) is not continuous, it averages 280 days a year. The low pH of this waste stream (approximately 2 to 4) is assimilated well when combined with the higher pH and volume of Influents A, B, and C. Characteristics of the waste

TABLE 36. CHARACTERIZATION OF INFLUENT B_1

Parameter	Concentration (mg/ℓ)	Standard Deviation	Average Daily Loading kg/day	(lb/day)	Standard Deviation	Yearly* Loading kg/year
TOC	4869	2367	13418	(29581)	3583	4904545
COD	20568	12669	47000	(103617)	22698	17227272
NH_3-N	1.36	0.453	6.5	(14.3)	1.6	2356
Total N	203	80.3	641	(1413)	476	234545
S^o	0.413	0.294	0.9	(2.0	0.5	326
SO_4	24.8	9.496	59	(130)	54	21455
P^o	136	59.2	405	(893)	206	148181

*Extrapolated from 6 months data.

TABLE 37. CHARACTERIZATION OF INFLUENT B (mg/ℓ)

Parameter	1975		1976	
	Average	Range	Average	Range
TOC	613	205 - 953	419	203 - 1067
COD	1769	598 - 2599	1253	614 - 3370
BOD	765	309 - 1243	623	285 - 1825
TSS	100	45 - 137	38	14 - 77
VSS	70	27 - 101	24	9 - 48
TDS	6740	3387 - 8263	2850	2138 - 4127
Chloride	1657	966 - 2238	743	574 - 1064
Sulfide	11.4	2.2 - 39.7	9.3	0.3 - 19.2
Phosphorus	48.2	18.4 - 68.0	17.2	7.7 - 54.0
Oil & grease	5.8	2.5 - 12.7	4.1	1.4 - 11.0
Phenol	2.36	0.79 - 8.6	0.76	0.44 - 1.15
NH_3-N	31.3	13 - 50	8.08	4.31 - 12.35
Chromium	2.51	1.58 - 3.5	2.68	1.0 - 3.85

TABLE 38. CHARACTERIZATION OF INFLUENT B LOADING VALUES (kg/day)

	1975				1976			
Parameter	Average kg/day	lb/ day	Standard Deviation	kg/year	Average kg/day	lb/ day	Standard Deviation	kg/year
TOC	3314	(7306)	2204	1199227	1173	(2586)	1324	428136
COD	1000	(2205)	6332	3515090	3550	(7826)	4187	1304363
BOD	4286	(9449)	3021	1551954	1768	(3898)	2241	646848
TSS	532	(1173)	336	194227	109	(240)	113	39939
VSS	377	(831)	240	137727	68	(150)	73	25090
TDS	35477	(78213)	20666	1287727	5509	(12145)	3311	1995954
Cl^-	8168	(18007)	3951	2616681	1436	(3166)	844	519818
S	41	(90)	32	139500	23	(51)	24	8485
P	273	(602)	181	141410	50	(110)	64	17903
Oil and grease	45	(99)	59	167545	10	(22)	9	4136
Phenol	12	(26)	14	3945	1.9	(4.2)	1.4	711
NH_3-N	145	(320)	77	5777	21	(46)	14	7818
Chromium	10	(22)	7		6.8	(15)	3.6	2473

TABLE 39. CHARACTERIZATION OF INFLUENT C (mg/ℓ)

Parameters	1975		1976	
	Average	Range	Average	Range
TOC	430	282 - 694	446	295 - 651
COD	1050	774 - 1353	1163	853 - 1558
BOD	584	406 - 715	682	534 - 920
TSS	24	16 - 39	33	17 - 87
VSS	13	8 - 18	15	9 - 28
TDS	5520	1249 - 7838	5878	3980 - 8719
Cl^-	1217	1079 - 1618	1185	825 - 1745
p^o	5.73	0.47 - 13.0	0.37	0.02 - 1.39
NH_3-N	121.8	40.1 - 335	98.4	32.0 -196.6
TKN	134.5	73.0 -259.2	118.4	44.7 -212.1
Oil and grease	2.32	0.7 - 5.5	2.1	1.0 - 4.9
Phenol	0.78	0.45 - 1.8	0.86	0.31 - 1.4
Fluoride	0.55	0.8 - 1.9	0.15	0.059- 0.56
Chromium	1.25	0.056- 2.06	0.92	0.47 - 3.15

TABLE 40. CHARACTERIZATION OF INFLUENT C LOADING VALUES (kg/year)

	1975				1976			
Parameter	Average kg/day	lb/ day	Standard Deviation	kg/year	Average kg/day	lb/ day	Standard Deviation	kg/year
TOC	4636	(10220)	1506	1549277	6455	(14230)	3482	2363973
COD	11227	(24751)	2395	3746033	16266	(35860)	7883	4877781
BOD	6227	(13728)	1429	2077031	9394	(20710)	3837	3124757
TSS	436	(961)	517	138978	446	(983)	245	162564
VSS	140	(309)	40	45193	208	(459)	73	7495
TDS	30413	(67049)	34763	20340234	83837	(184829)	38673	30614904
Cl^-	12782	(28179)	1007	3933245	16665	(36740)	6319	6102695
P^o	59	(130)	45	16832	5	(11)	5	1713
NH_3-N	1229	(2709)	581	406784	1347	(2970)	626	495695
TKN	1501	(3309)	671	413168	1769	(3900)	1488	652320
Oil and grease	25	(55)	16	8511	32	(71)	24	11222
Phenol	8	(18)	2.9	2606	13	(29)	9	4664
Fluoride	13.4	(30)	3.9	40830	2.3	(5.1)	2.7	855
Chromium	5	(11)	10	701	12	(26)	9	4754

stream are low organic content and high phosphorus and nitrogen content. Tables 41 and 42 show the characteristic concentration and loading values for Influent D.

Treatability of Wastewater

There are certain requirements for the successful biological treatment of industrial wastewaters. These are:

- Wastewater constituents in a form amenable to biodegradation
- Wastewater temperature in the 4 to 40°C range
- pH between 6 and 9
- Adequate nutrients available for biological metabolism and cell synthesis
- Suppression of toxic or inhibitory materials through removal, dilution, or inactivation.

In initial studies on the wastewater from the Texas City petrochemical plant, engineers at Dicharger 1 determined that the wastewaters were amenable to biodegradation, and with pretreatment and nutrient addition, the wastewater satisfied the above mentioned criteria.

Typical treatment of petrochemical wastewater involves aerobic biological systems, in particular, activated sludge and aerated stabilization processes. The high waste temperatures and high oxygen demand rates of petrochemical wastewater require additional expenditures to aerate the system and dispose of produced biological solids. Concern over these problems led engineers to investigate possible anaerobic treatment of petrochemical wastewaters. Anaerobic treatment is advantageous in areas with warm, mild climates and land available for large lagoons needed for anaerobic stabilization. The advantages and disadvantages of anaerobic treatment, as determined by Discharger 1, are shown in Table 43.

Three anaerobic treatment processes were selected for study:

- Anaerobic contact digester
- Anaerobic trickling filter
- Anaerobic lagoon.

The characteristics of these three systems, all first tested in bench-scale, are shown in Table 44.

Anaerobic biodegradation of materials takes place in two stages: (1) organic reduction to volatile acids, and (2) methanogenesis of the volatile acids. Organic material in both the anaerobic contact digester and trickling filter showed degradation

TABLE 41. CHARACTERIZATION OF INFLUENT D (mg/ℓ)

Parameters	1975		1976	
	Average	Range	Average	Range
TOC	41.62	17.6 - 92	35.37	19 - 50
COD	137.67	88.2 - 277	111.13	67.4 - 192
BOD	16.346	1.5 - 90.5	9.03	4 - 14
TSS	28.69	18.8 - 62	29.11	16 - 48.7
VSS	12.68	6.25 - 21.5	14.91	8.3 - 23
TDS	7056.6	5606 - 7890	5514	3593 -10152
Cl^-	698.44	520 - 900	563.3	425 -733.3
P	909.88	623 - 1150	566.06	2022 - 1530
Sulfide	374.66	223 - 571		
NH_3-N	306.13	95 - 546	490.19	260 - 1350
Fluoride	19.91	6.4 - 31.6	15.03	10.5 - 21.9

TABLE 42. CHARACTERIZATION OF INFLUENT D LOADING VALUES (kg/year)

	1975				1976			
Parameter	Average kg/day	lb/day	Standard Deviation	kg/year	Average kg/day	lb/day	Standard Deviation	kg/year
TOC	30	(66)	18.8	10804	21	(46)	12.4	7649
COD	96	(212.)	48	34863	67	(148)	41.8	24473
BOD	12	(26)	22	4305	5.8	(13)	3	2111
TSS	52	(115)	82	7420	17	(37)	11.1	6375
VSS	9	(20)	3.3	2988	10	(22)	6.1	3682
TDS	4870	(10737)	1284	2229032	3288	(7249)	1749	2114929
Cl^-	484	(1067)	138	176463	327	(722)	130	190742
P	624	(1376)	248	227770	351	(774)	414	128134
S	247	(545)	80	9008				
NH_3-N	199	(439)	143	72219	288	(635)	195	105762
Fluoride	13	(29)	8.6	4862	9.3	(21)	4.3	3404

TABLE 43. TREATMENT CONSIDERATIONS AT GCWDA 40-ACRE PLANT(66)

I. Advantages of Anaerobic Processes

A. No aeration equipment is required for organic reduction. Associated capital, power, and maintenance costs are avoided. System loading is not limited by oxygen transfer.

B. Cellular material is produced in lower quantity and more stable form. Savings in nutrients and in flocculants, equipment, and labor costs for biomass dewatering and final disposal can be realized.

C. Some problem organic chemicals difficult to degrade aerobically will degrade anaerobically.

D. The oxygen in nitrate and sulfate ions can be utilized for organic oxidation.

E. Methane in off-gas potentially can be used for heating or in odor control by incineration.

F. The anaerobic system can operate at temperatures at which a flocculant aerobic system experiences biomass separation difficulties.

II. Potential Problems with Anaerobic Processes

A. High temperatures are needed for maximum rates.

B. High biomass concentration is required for reasonable rates at short retention times.

C. Regeneration time for methane bacteria is long (2 to 11 days at 37°C), thereby requiring long solids retention and acclimation times.

D. Methanogenic microorganisms are reportedly more sensitive to shock loads, toxic materials, and environmental conditions.

E. Effluents low in BOD (<50 mg/l) with good aesthetic properties are difficult to produce.

F. Produced gases are odorous if released.

TABLE 44. SYSTEMS STUDIED FOR APPLICATION AT 40-ACRE (66)

	Submerged Filter	Contact Digester	Open Lagoon
Description	Rock or gravel packed column	Completely mixed vessel	Basin with considerable stratification
Flow pattern	Plug flow	Backmixed	Some wind and wave mixing, thermal turnovers
Biosolids level	High biomass through attached growths	High biomass through settling and return	Low suspended solids, bottom sludge layer
Metabolic pathways	Fermentation and anaerobic respiration	Fermentation and anaerobic respiration	Fermentation, anaerobic respiration, sulfur oxidation, photosynthesis, some aerobic respiration
Retention time	1 to 3 days	1 to 10 days	10 to 100 days
Gas collection	Normally collected	Collected	Gas is released, although a plastic covering with peripheral collection tiles is possible
Temperature control	Not normally practiced	Usually practiced	Unfeasible unless covered and insulated

to volatile acids. However, methane production was inadequate in both cases, because of (1) inadequate retention time for generation of methanogenic bacteria, or (2) volatile acid or sulfide concentrations inhibiting the system. The anaerobic lagoon did not show these complications.

The most promising system, the anaerobic lagoon, was developed into a pilot-scale demonstration unit to optimize the process and provide economic and design data adaptable for a large-scale plant. Pilot-scale aerobic treatment studies were made of the effluent from the anaerobic unit. These studies provided information for designing and estimating the cost of a total treatment plant combining the roughing anaerobic treatment with the polishing aerobic treatment. Facultative lagoons added after the aerobic treatment provide a long retention time and large area for solids separation and subsequent storage and anaerobic decomposition of the solids. Figure 16 shows the final demonstration system schematic.

GCWDA made an agreement with Dischargers 1 and 2 to construct and operate a full-scale biological treatment system to treat the petrochemical wastewater.

For biological treatment of wastewater, biodegradable organics and nutrients need to have a BOD/N/P weight ratio of approximately 100/5/1 (58). The combined values of Influents A, B, and C and their relationship to required nutrients (Table 45) show the combined waste streams to be deficient in phosphorus. GCWDA, to negate phosphorus nutrient addition, contracted with Discharger 3 to treat the runoff water from the latter's phosphate fertilizer storage area. The inclusion of this waste stream satisfied the 40-Acre phosphorus requirements (Table 46).

REGULATORY REQUIREMENTS

Influents and effluent from the GCWDA 40-Acre facility are under the jurisdication of the National Pollution Discharge Elimination System (NPDES), as administered by the Texas Water Quality Board (TWQB). Monitoring requirements for Dischargers 1 and 2 are shown in Table 47 and for Discharger 3 in Table 48. In addition, there are specific influent limitations covered under the permit (Table 49).

TREATMENT SYSTEM CONSTRUCTION AND DESIGN

The GCWDA 40-Acre treatment system consists of:

- pH adjustment (HCl)
- Nutrient addition (H_3PO_4, NH_3)
- Emergency spill diversion

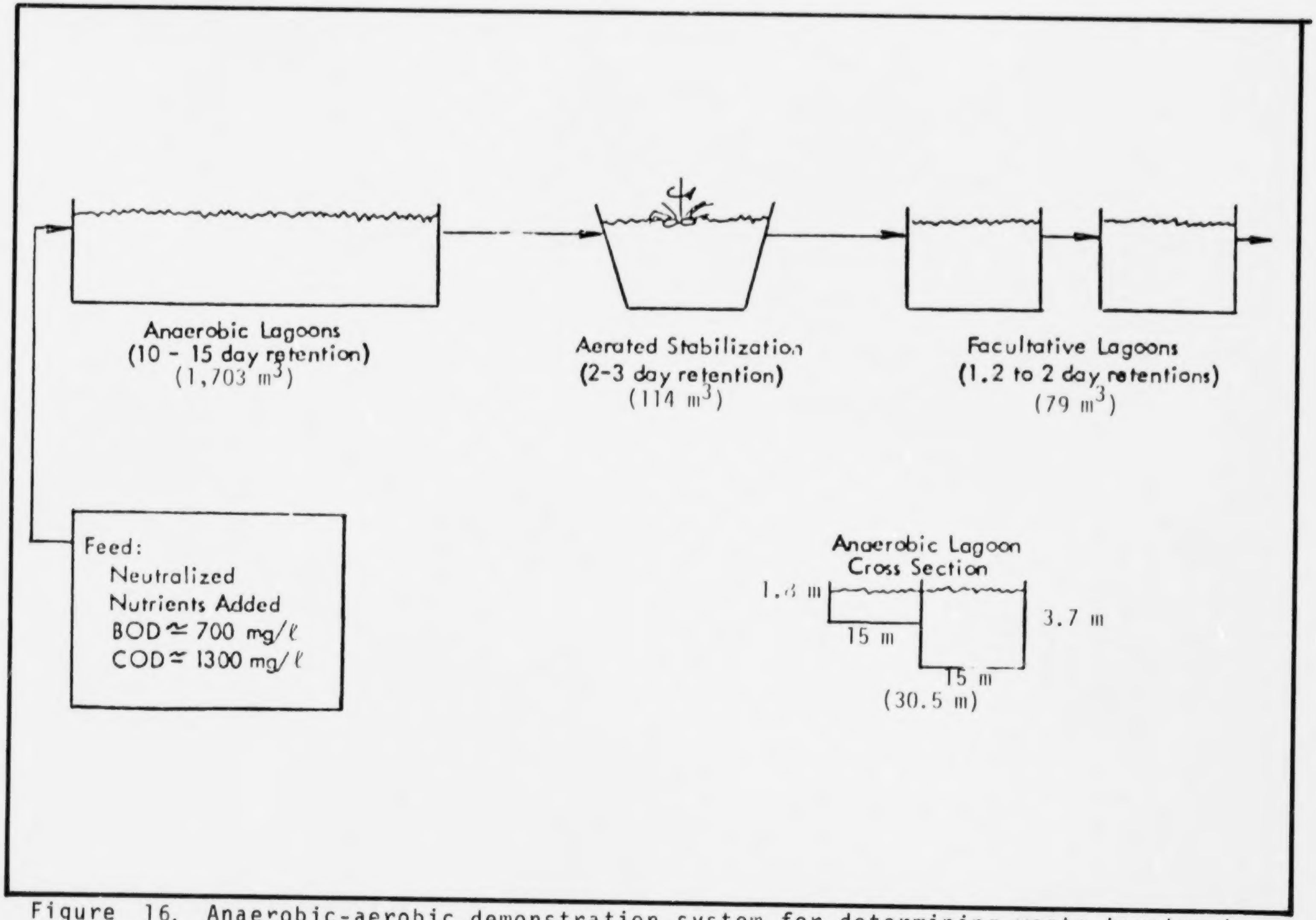

Anaerobic Lagoons
(10 - 15 day retention)
(1,703 m³)
Aerated Stabilization
(2-3 day retention)
(114 m³)
Facultative Lagoons
(1.2 to 2 day retentions)
(79 m³)
Feed:
Neutralized
Nutrients Added
BOD ≃ 700 mg/ℓ
COD ≃ 1300 mg/ℓ
Anaerobic Lagoon
Cross Section
1.8 m
15 m
3.7 m
15 m
(30.5 m)

Figure 16. Anaerobic-aerobic demonstration system for determining waste treatment design at 40-Acre (66)

TABLE 45. COMBINED INFLUENT A, B, AND C LOADING VALUES* AND THEIR RELATIONSHIP TO REQUIRED NUTRIENTS

	BOD	COD	Phosphorus	Nitrogen
Influent A	17000	33000	154	336
Influent B	1770	3540	50	23
Influent C	9390	16280	4.5	1770
Total	28160	52820	209	2129

Required BOD/N/P weight ratio 100/5/1

Available BOD/N/P weight ratio 100/7.5/0.7

* Average kg/day

TABLE 46. COMBINED INFLUENT A, B, C, AND D LOADING VALUES* AND THEIR RELATIONSHIP TO REQUIRED NUTRIENTS

	BOD	COD	Phosphorus	Nitrogen
Influent A	17000	33000	150	336
Influent B	1770	3540	50	23
Influent C	9390	16280	4.5	1770
Influent D	5.9	68	350	288
Total	28166	52888	555	2417

Required BOD/N/P weight ratio 100/5/1

Available BOD/N/P weight ratio 100/8.5/2

* Average kg/day 1976 data

TABLE 47. DISCHARGERS 1 AND 2 INFLUENT MONITORING REQUIREMENTS

Characteristic	Measurement Frequency	Sample Type
BOD_5	Daily	24-hr. composite
COD	Daily	24-hr. composite
TSS	Daily	24-hr. composite
Oil and Grease	3/week	Grab
NH_3-N	Daily	24-hr. composite
Chromium	1/week	24-hr. composite
Phenols	2/week	24-hr. composite
R-Cl	1/week	24-hr. composite
Phosphorus	2/month	24-hr. composite
Fluoride	2/month	24-hr. composite
Cyanide	2/month	24-hr. composite
Mercury	2/month	24-hr. composite
Lead	2/month	24-hr. composite
Arsenic	2/month	24-hr. composite
TKN	2/month	24-hr. composite
Flow	Continuous	Record
Temp.	Continuous	Record
pH	Continuous	Record

TABLE 48. DISCHARGER 3 INFLUENT MONITORING REQUIREMENTS

Characteristic	Measurement Frequency	Sample Type
BOD_5	Daily	24-hr. composite
COD	Daily	24-hr. composite
TSS	Daily	24-hr. composite
Oil and Grease	3/week	Grab
NH_3-N	Daily	24-hr. composite
Chromium	1/week	24-hr. composite
Phenols	N/A	N/A
R-Cl	N/A	N/A
Phosphorus	2/month	24-hr. composite
Fluoride	2/month	24-hr. composite
Cyanide	1/3 months	24-hr. composite
Mercury	1/3 months	24-hr. composite
Lead	1/3 months	24-hr. composite
Arsenic	1/3 months	24-hr. composite
TKN	1/3 months	24-hr. composite
Flow	Daily	Estimated
Temp.	Daily	Grab
pH	Daily	Grab

TABLE 49. DISCHARGERS 1, 2, AND 3 INFLUENT LIMITATIONS IN KG/DAY (LB/DAY) EFFECTIVE JULY 1, 1977

	Discharge 1		Discharge 2		Discharge 3	
Characteristic	Daily avg.	Daily max.	Daily avg.	Daily max.	Daily avg.	Daily max.
Total chromium	15.3 (33.7)	30.7 (6.77)	1.1 (2.4)	2.3 (5.1)	0.20 (0.44)	0.40 (0.88)
Aliphatic chlorinate hydrocarbon	0.33 (0.72)	0.66 (1.45)	2.0 (4.4)	4.0 (8.8)	N/A	N/A
Cyanide	N/A	N/A	4.6 (10.1)	9.3 (20.5)	N/A	N/A
Fluoride	N/A	N/A	N/A	N/A	15*	30*

N/A - Not available

* mg/ℓ

- Equalization

- Anaerobic, limited aerobic, aerobic and facultative biological treatment.

Figure 17 shows a schematic diagram of the facility's layout and Table 50 the dimensions and retentions of the basins.

The facility design was based upon an extensive laboratory and pilot study of anaerobic treatment of petrochemical wastewaters. The study was conducted by Discharger 1 during the late 1960's and early 1970's; a summary of the design findings is presented later in this chapter. The treatment system was designed for a primary treated petrochemical wastewater with maximum values as follows: flow, 5.1 x 10^4 m^3/day (13 MGD); loading, 59,000 kg/day BOD (130,072 lb/day); and 118,000 kg/day (260,145 lg/day) COD.

Construction

The facility basins were excavated by balance cut and fill. Basin slopes are two horizontal units for each vertical unit. To control wave erosion of the embankment all earthen basins are lined with 10 cm (4-in) of concrete from the crest of the slope to 61 cm (3-ft) below the water surface. The impermeability of the clay-rich soil made complete lining of the basins unnecessary. The berms are topped by a roadway, approximately 3.6 m (12-ft) wide. The entire facility is enclosed by a 1.8 m (6-ft) high chain link fence topped by three strands of barbed wire. The area is lighted by 30 utility pole-mounted high intensity lamps. The facility operates continuously.

The four waste streams currently treated at the facility (Influents A, B, C, and D) are transported there in individual pipelines. Influent enters the facility at two points (Figure 17): Influents A, B, and C at influent point 1; Influent D, because of its high sulfur content, enters at influent point 2, bypassing the anaerobic lagoons. Influent flow measurements are determined by venturi (differential pressure) meters inserted in the pipelines.

Chemicals for pH adjustment (HCl) and nutrient addition (H_3PO_4 and NH_3)are stored in tanks adjacent to influent point 1 (Figure 17).

Figure 18 shows the distribution piping within the facility. The flexibility of this system allows various retention periods and treatment schemes, depending upon influent loading and composition. Basin interconnect piping is low-head corrugated metal drainage pipe with a protective coating. Liquor flow through the system is gravitational. There are no provisions for returning settled biomass from the facultative lagoons to the aerated stablilization basins.

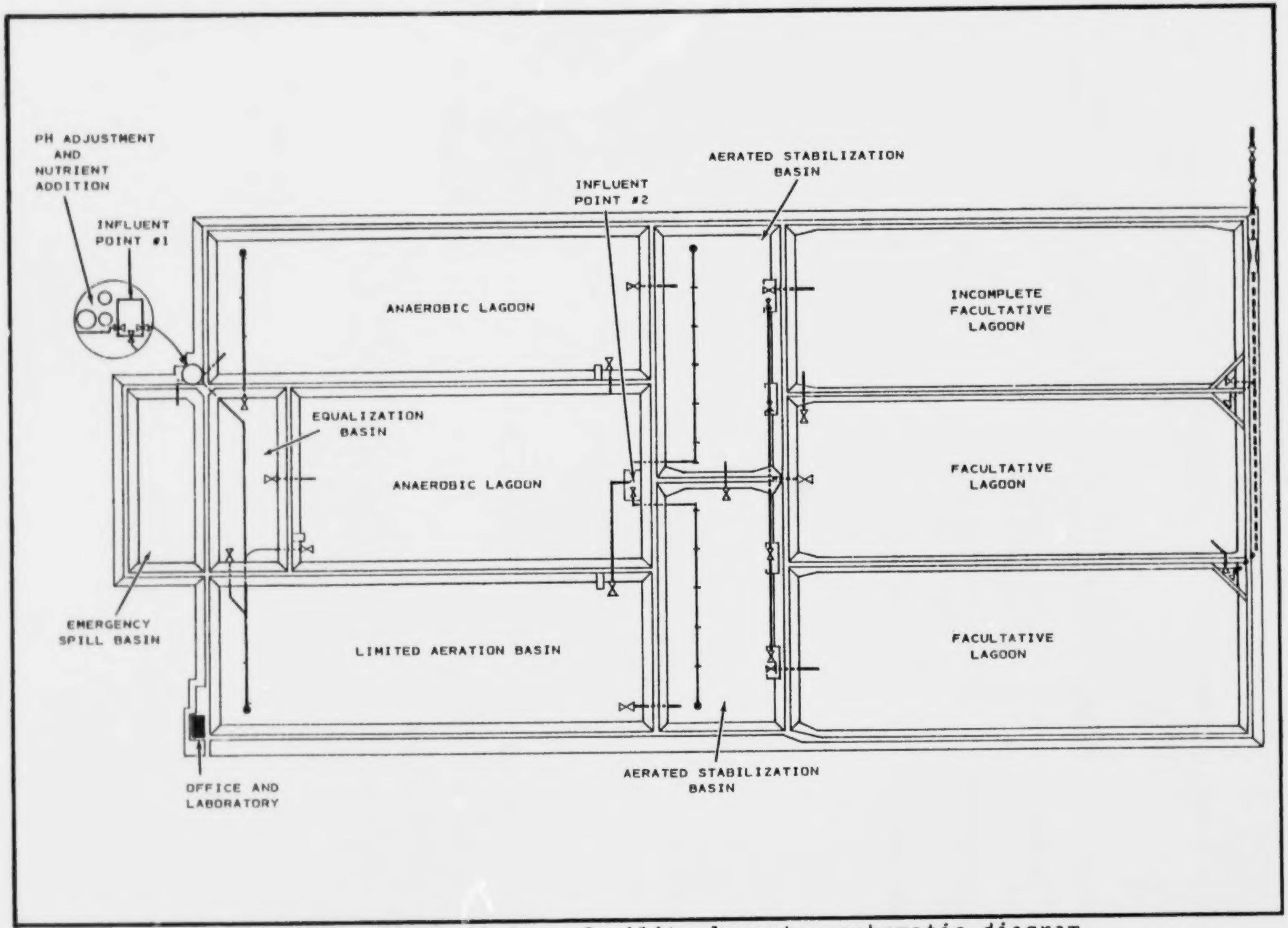

PH ADJUSTMENT
AND
NUTRIENT
ADDITION
INFLUENT
POINT #1
ANAEROBIC LAGOON
EQUALIZATION
BASIN
ANAEROBIC LAGOON
EMERGENCY
SPILL BASIN
LIMITED AERATION BASIN
OFFICE AND
LABORATORY
INFLUENT
POINT #2
AERATED STABILIZATION
BASIN
AERATED STABILIZATION
BASIN
INCOMPLETE
FACULTATIVE
LAGOON
FACULTATIVE
LAGOON
FACULTATIVE
LAGOON

Figure 17. GCWDA 40-Acre facility layout: schematic diagram.

TABLE 50. 40-ACRE BASIN DIMENSIONS AND RETENTION

Basin	Number	Dimensions in meters (ft)*	Capacity 10^3 m^3 (mg^1)	Retention days†
Emergency spill	1	188x56x4.0 (618x184x13)	42 (11)	<1
Equalization	1	188x56x4.0 (618x184x13)	42 (11)	<1
Anaerobic	2	430x154x4.0 (1410x506x13) 372x188x4.0 (1220x618x13)	265 (70)	5
Limit aeration	1	430x154x4.0 (1410x506x13)	265 (70)	5
Aerated stabilization	2	248x125x2.4 (815x410x8)	76 (20)	1.5
Facultative	3	445x166x2.6 (1460x545x9)	189 (50)	3.7

Total basin acreage - 50.6 ha (125 ac)

---

[*] Length x width x depth.

[†] At maximum design flow: 51,100 m^3/D (13.5 MGD).

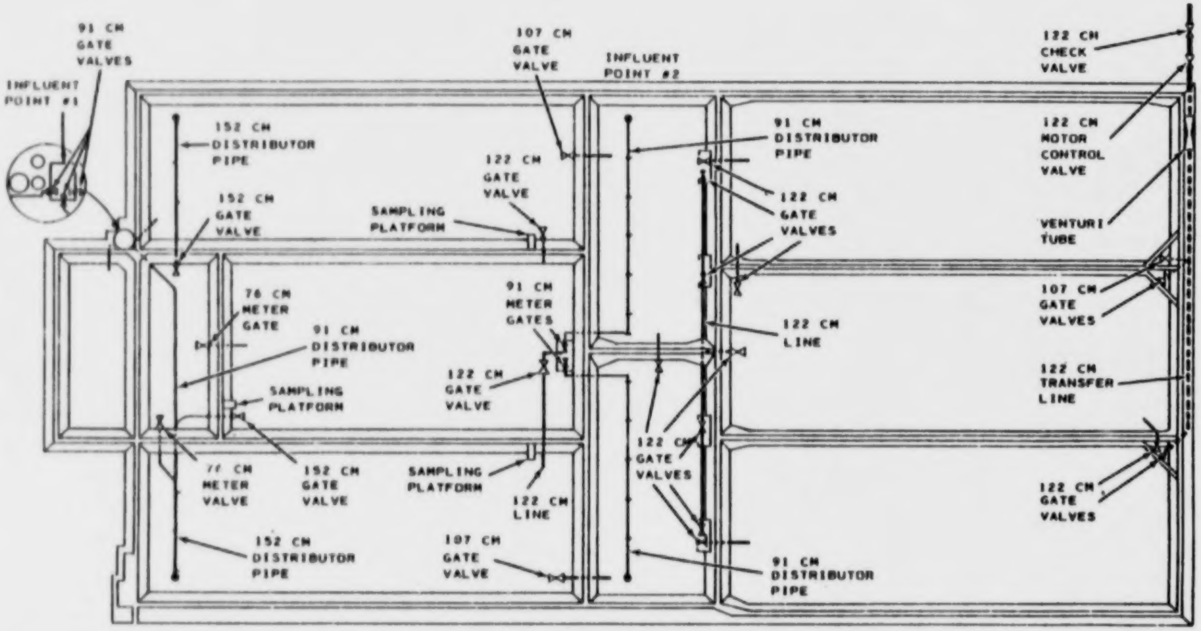

91 CM GATE VALVES
INFLUENT POINT #1
152 CM DISTRIBUTOR PIPE
152 CM GATE VALVE
76 CM METER GATE
91 CM DISTRIBUTOR PIPE
SAMPLING PLATFORM
76 CM METER VALVE
152 CM GATE VALVE
152 CM DISTRIBUTOR PIPE
107 CM GATE VALVE
122 CM GATE VALVE
SAMPLING PLATFORM
91 CM METER GATES
122 CM GATE VALVE
SAMPLING PLATFORM
122 CM LINE
107 CM GATE VALVE
INFLUENT POINT #2
91 CM DISTRIBUTOR PIPE
122 CM GATE VALVES
122 CM LINE
122 CM GATE VALVES
91 CM DISTRIBUTOR PIPE
122 CM CHECK VALVE
122 CM MOTOR CONTROL VALVE
VENTURI TUBE
107 CM GATE VALVES
122 CM TRANSFER LINE
122 CM GATE VALVES

Figure 18. 40-Acre distribution piping.

Sampling platforms are located at each of the anaerobic lagoons and at the limited aeration lagoon. Wastewater testing and maintenance duties are handled in the laboratory and office building located at the facility.

The facility uses the Ashbrook Mechanical Surface Aerator-High Speed (MSAH) Model 75/900 (75 hp, 900 rpm) for oxygen transfer and maintenance of solids suspension. Figure 19 shows a schematic of the aerator, and Table 51 gives the aerator characteristics. There are 50 such aerators at the facility: 14 in the limited aeration basin and 18 in each aerated stabilization basin. Each aerator is moored to wooden pilings by cables.

Summary of Discharger 1 Study into Petrochemical Wastewater Treatment

During the late 1960's and early 1970's, Discharger 1 made extensive laboratory and pilot study into the biological treatment of petrochemical wastewater. A system design was used that incorporated anaerobic, aerated stabilization and facultative treatment. A summary of the findings follows; a more complete discussion of the research that preceded the design is included in Reference 66.

Anaerobic Lagoons--

The anaerobic lagoons provide waste equalization and cooling as well as removal of inhibitory material and a portion of influent oxygen-demanding materials.

The anaerobic degradation of petrochemical wastewater organics was found to vary both with temperature and volumetric loading rate (mass of organics applied/unit volume-time). Degradation was greatest at warm temperatures and light loading rates and decreased with either a temperature drop or a loading increase. Figure 20 shows COD removal as a function of volumetric loading and temperature. The area under the COD percentage removal line represents temperature and loading conditions that can be expected to have COD removal values of that level or greater. For example, at a COD loading of 160 kg COD/1,000 m^3 (10 lb/1,000 ft^3) and a wastewater temperature of 30°C, a COD removal of 55 percent or greater is expected. The retention time required to arrive at these removal values can be computed from the following equation:

$$\text{Retention (days)} = \frac{\text{Influent concentration (mg/}\ell\text{)}}{\text{Desired loading (mg/}\ell\text{/day)}}$$

Percent BOD removal in the anaerobic lagoon showed a significant correlation with percent COD removal (Figure 21).

The depth of the anaerobic lagoon was found to have an effect upon sulfide concentration in the lagoon; effects of

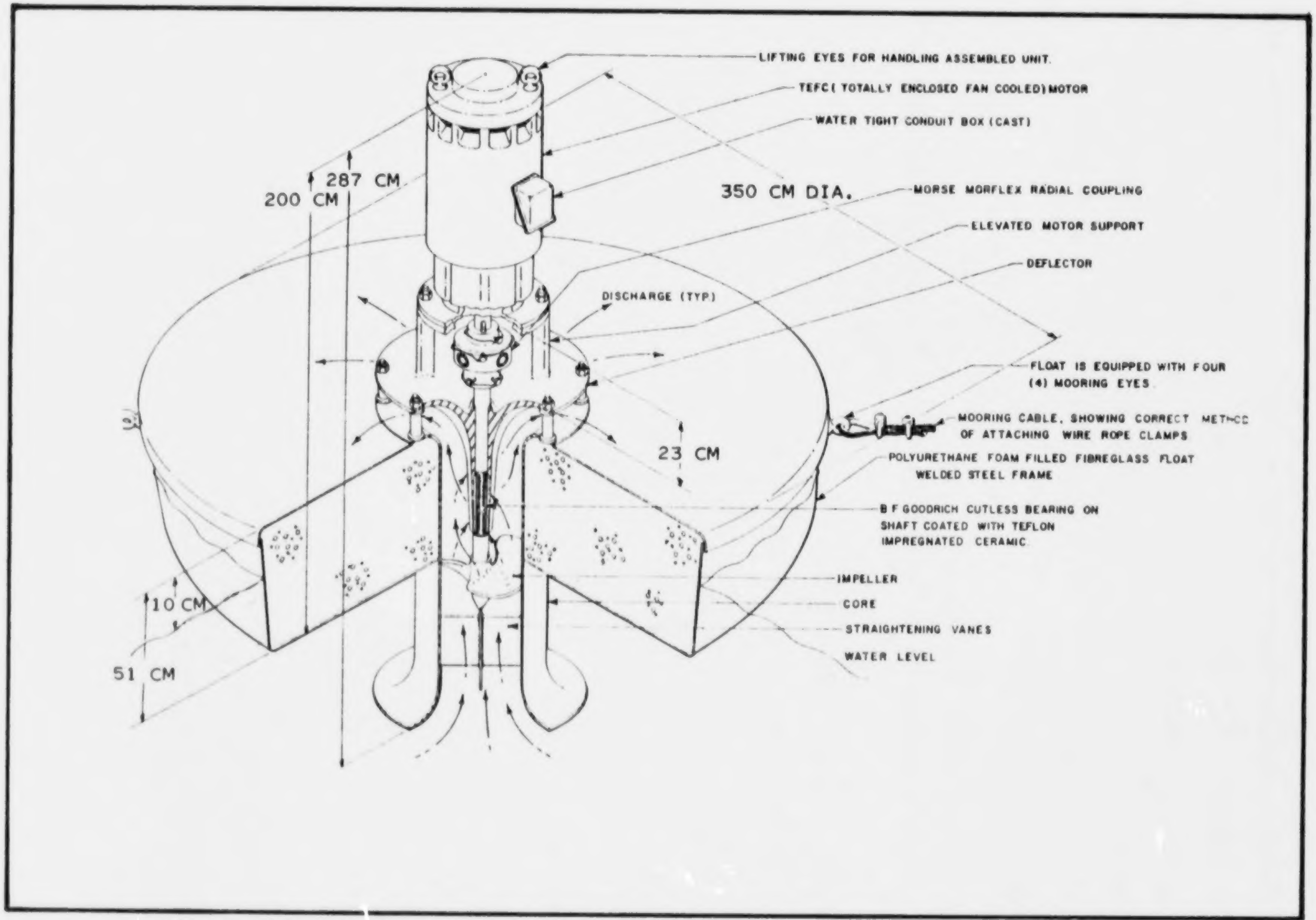

LIFTING EYES FOR HANDLING ASSEMBLED UNIT.
TEFC (TOTALLY ENCLOSED FAN COOLED) MOTOR
WATER TIGHT CONDUIT BOX (CAST)
287 CM
200 CM
350 CM DIA.
MORSE MORFLEX RADIAL COUPLING
ELEVATED MOTOR SUPPORT
DEFLECTOR
DISCHARGE (TYP)
FLOAT IS EQUIPPED WITH FOUR (4) MOORING EYES
MOORING CABLE, SHOWING CORRECT METHOD OF ATTACHING WIRE ROPE CLAMPS
POLYURETHANE FOAM FILLED FIBREGLASS FLOAT WELDED STEEL FRAME
23 CM
B F GOODRICH CUTLESS BEARING ON SHAFT COATED WITH TEFLON IMPREGNATED CERAMIC
IMPELLER
CORE
STRAIGHTENING VANES
WATER LEVEL
10 CM
51 CM

Figure 19. Ashbrook Mechanical Surface Aerator - High Speed (MSAH) 76 horsepower/900 rpm approximate weight - 2023 kg.

TABLE 51. ASHBROOK MSAH 75/900 CHARACTERISTICS

Oxygen transfer factor:[1]	1.3 kg O_2/HP-HR
Impingement diameter:[2]	13.1 m (43 ft)
Pumping rate:[3]	108.8 m^3/ min (28,740 gal/min)
Induced flow rate:[4]	438.7 m^3/ min (115,900 gal/min)
Diameter of surface area influence:[5]	122.8 m (403 ft)
Diameter of effective mixing:[6]	38.4 m (126 ft)

1 Under standard conditions of 1 atm, 20°C

2 The impingement diameter describes the spray pattern of the pumped liquid. This water is distributed through the atmosphere radially and horizontally in the form of countless small droplets and thin liquid envelopes for oxygen entrainment. The kinetics of the discharged liquid are utilized to move surface water away from the aerator for efficient mixing.

3 The pumping rate of an ASHBROOK MSAH Mechanical Aerator is the amount of liquid pumped through the pumping chamber.

4 The induced flow rate of an ASHBROOK MSAH Mechanical Aerator is the total influenced fluid which is pumped directly and/or kept in motion indirectly.

5 The diameter of surface area influence describes the general periphery of the upper liquid level containing dissolved oxygen. The diameter was calculted using 2.2 hp per 1,000 m^2 of lagoon surface area.

6 The diameter of effective mixing is determined by assuming a horsepower value per unit volume of the basin. This value can vary from 3.53 hp to 35.3 hp per 1,000 m^3 of basin depending upon the density of the suspended solids. The diameter of effective mixing was calculated using 17.7 hp per 1,000 m^3.

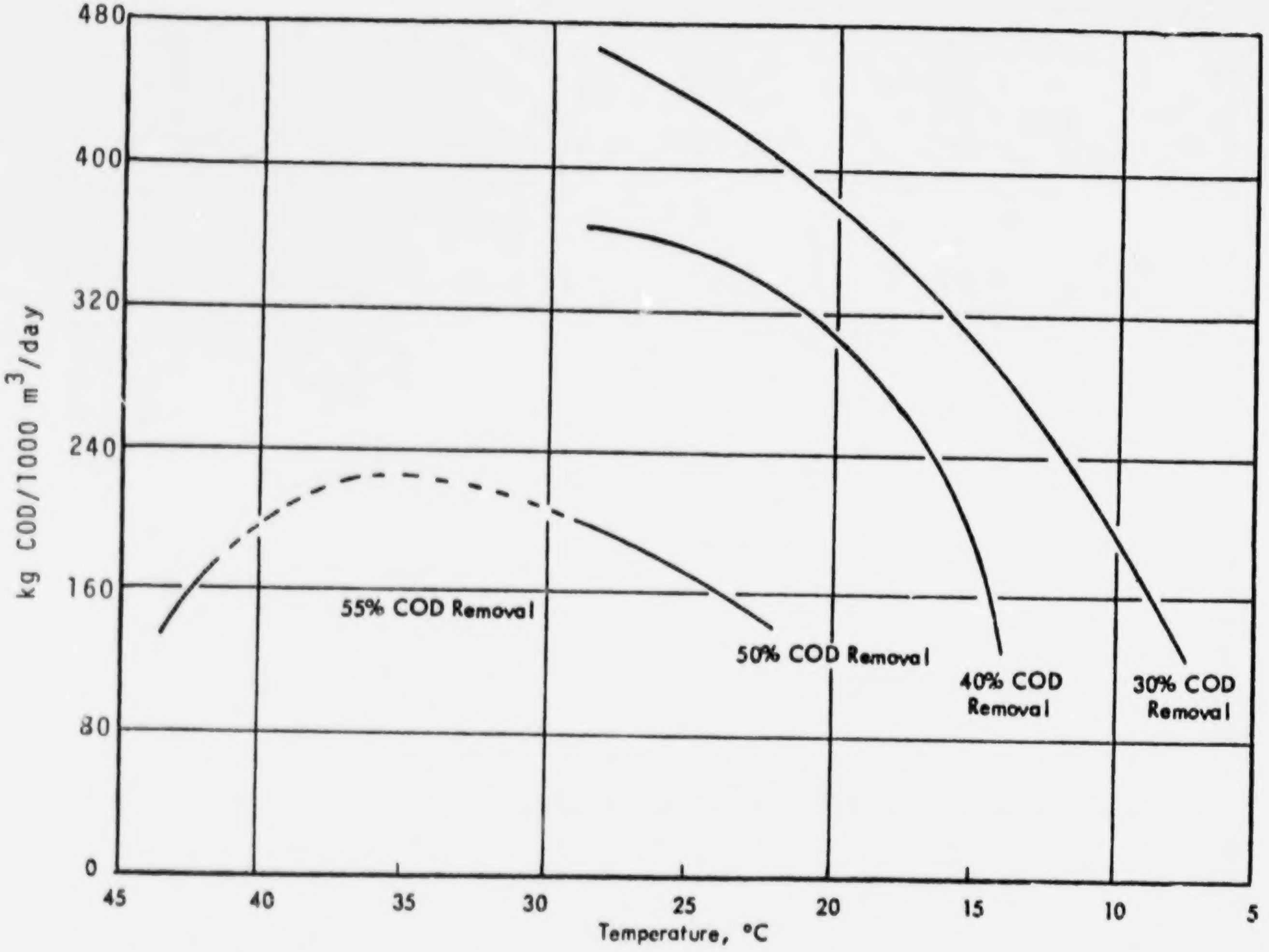


Figure 20. COD removal as a function of loading and temperature.

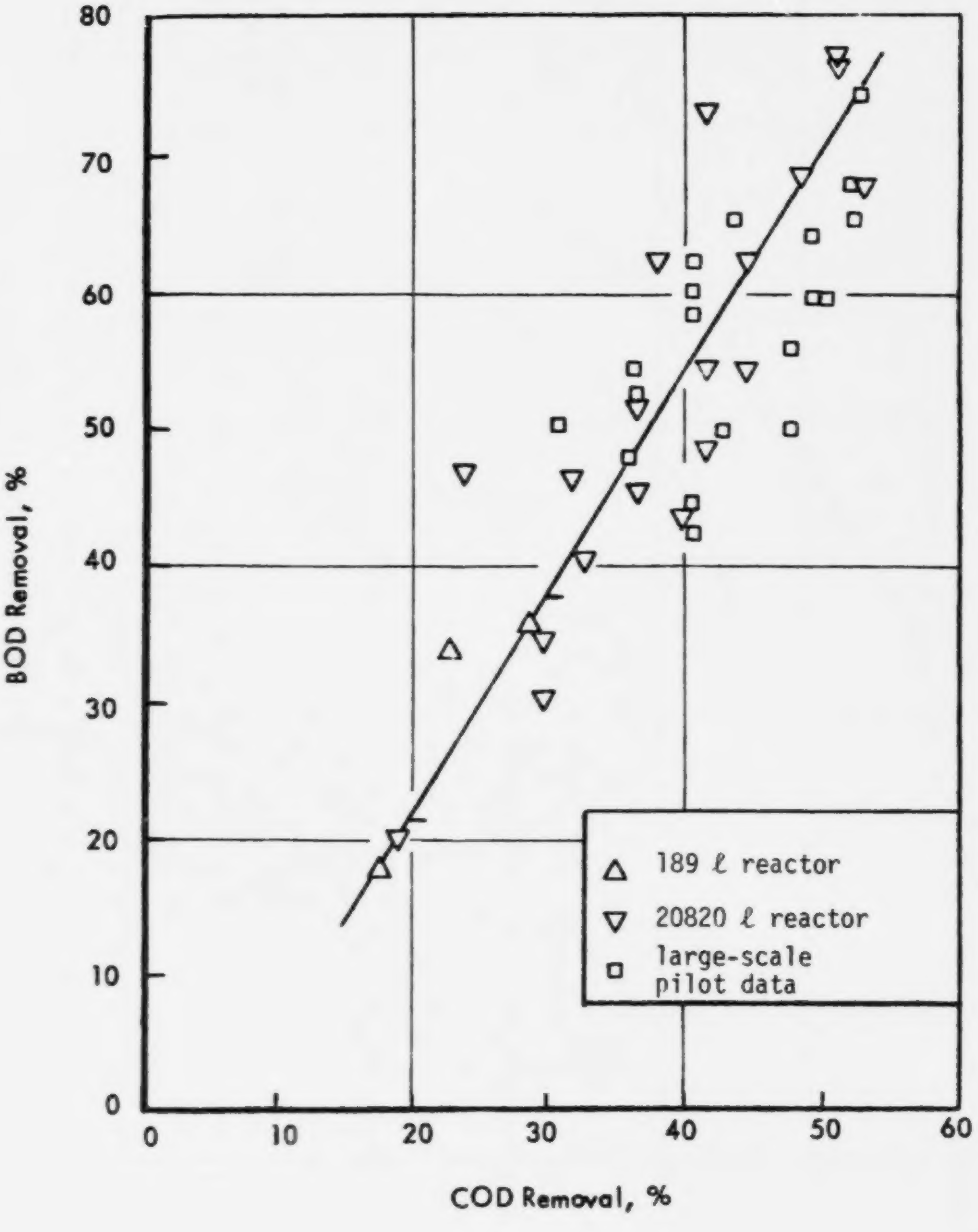


Figure 21. Relationship between BOD and COD removal.

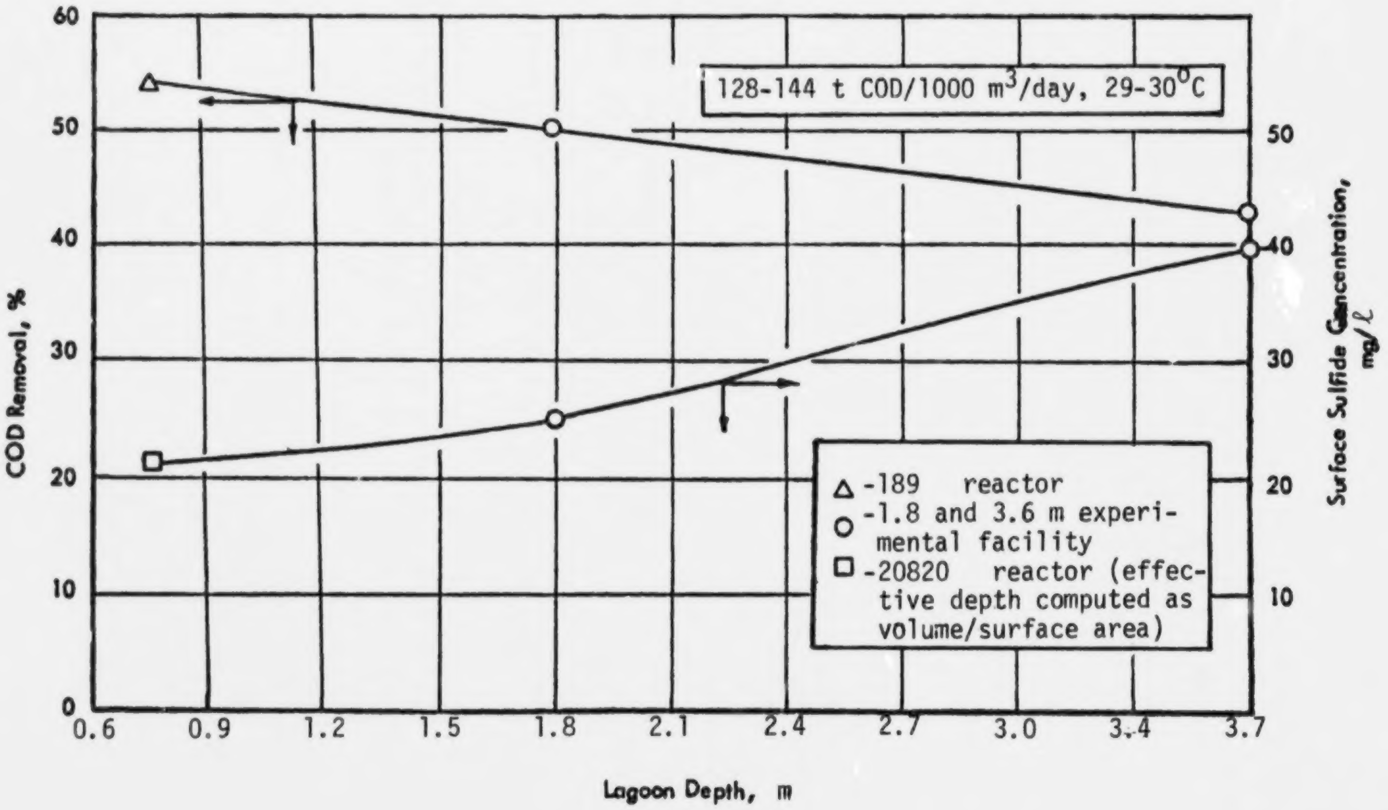


Figure 22. Effect of lagoon depth on COD removal and sulfide level.

depth on both COD removal and sulfide concentration are shown in Figure 22. Overall COD removal changed by only 11 percent with a fourfold increase in depth, whereas the surface sulfide level increased by a factor of two.

Aerated Stabilization--

Aerated stabilization was chosen to provide the additional treatment required for the anaerobic effluent. The aerated stabilization process is a high-rate lagooning operation employing a low concentration of nonflocculent bacteria synthesized during biooxidation of the organics and discharged with the effluent. Given a proper environment and lack of toxicants, the performance of an aerated stabilization process is limited by one of two factors. If the system is not operated at a positive oxygen level, removal is dependent upon the quantity of oxygen supplied. If oxygen is maintained above some level where performance is independent of oxygen concentration, the limiting mechanism is retention time for bacterial growth and resulting assimilation of waste products. If the rate of liquid flow through the reactor and resulting detention time is less than the time required for stabilization, only a portion of the waste will be removed. As the detention time becomes greater, near equilibrium stabilization is reached.

In order to determine the limiting oxygen level, a study was performed on a pilot aerated stabilization unit in which the oxygen level was controlled. At 1 mg/ℓ residual DO, the unit became dark and odorous. This condition was suggested to be due to incomplete conversion of sulfides, resulting in end products such as sulfite, thiosulfate or elemental sulfur (66). A DO residual of 1.5 mg/ℓ was found to be necessary to avoid odor problems and to maintain acceptable BOD and COD removals (70 and 60 percent, respectively).

The pilot unit was aerated continuously for up to 8 days to determine the optimum retention time for aerated stabilization (Figure 23). A three-day aeration period was found to be sufficient.

Facultative Lagoons--

The biosolids produced by the aerated stabilization lagoon are nonflocculent and consequently settle at a slow rate. Facultative lagoons were selected to provide a long retention time and a large area for solids separation, as well as for subsequent storage and anaerobic decomposition of the solids. After two days retention,removal of approximately 60 percent of the applied volatile and suspended solids from the wastewater stream was observed (Figure 24).

Two pilot-scale facultative lagoons were operated for a 231-day test period. During this time, 1,065 kg (2,348 lb) of total suspended solids (TSS) and 879 kg (1,938 lb) of volatile

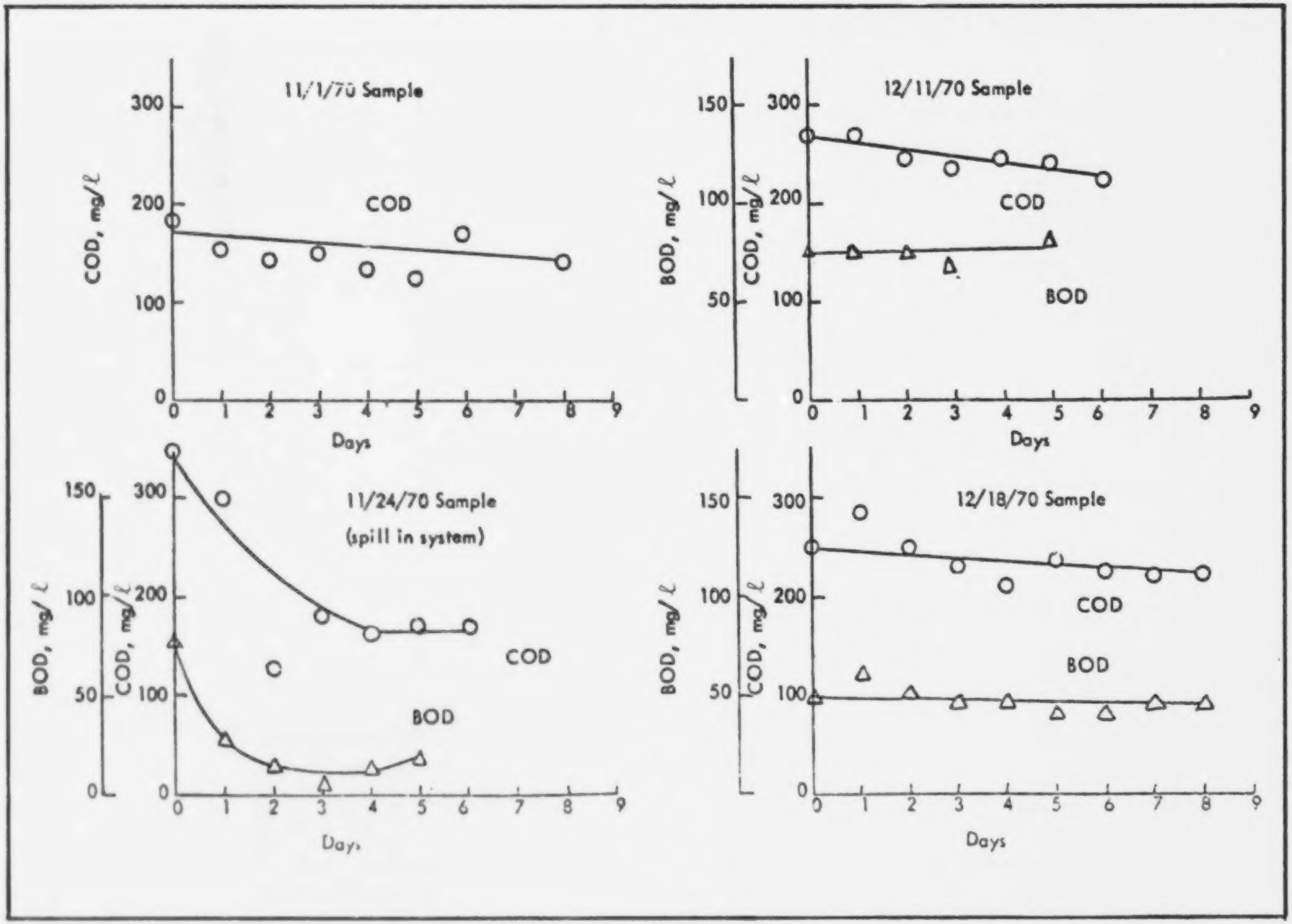


Figure 23. Effect of additional aeration on aerated stabilization effluent.

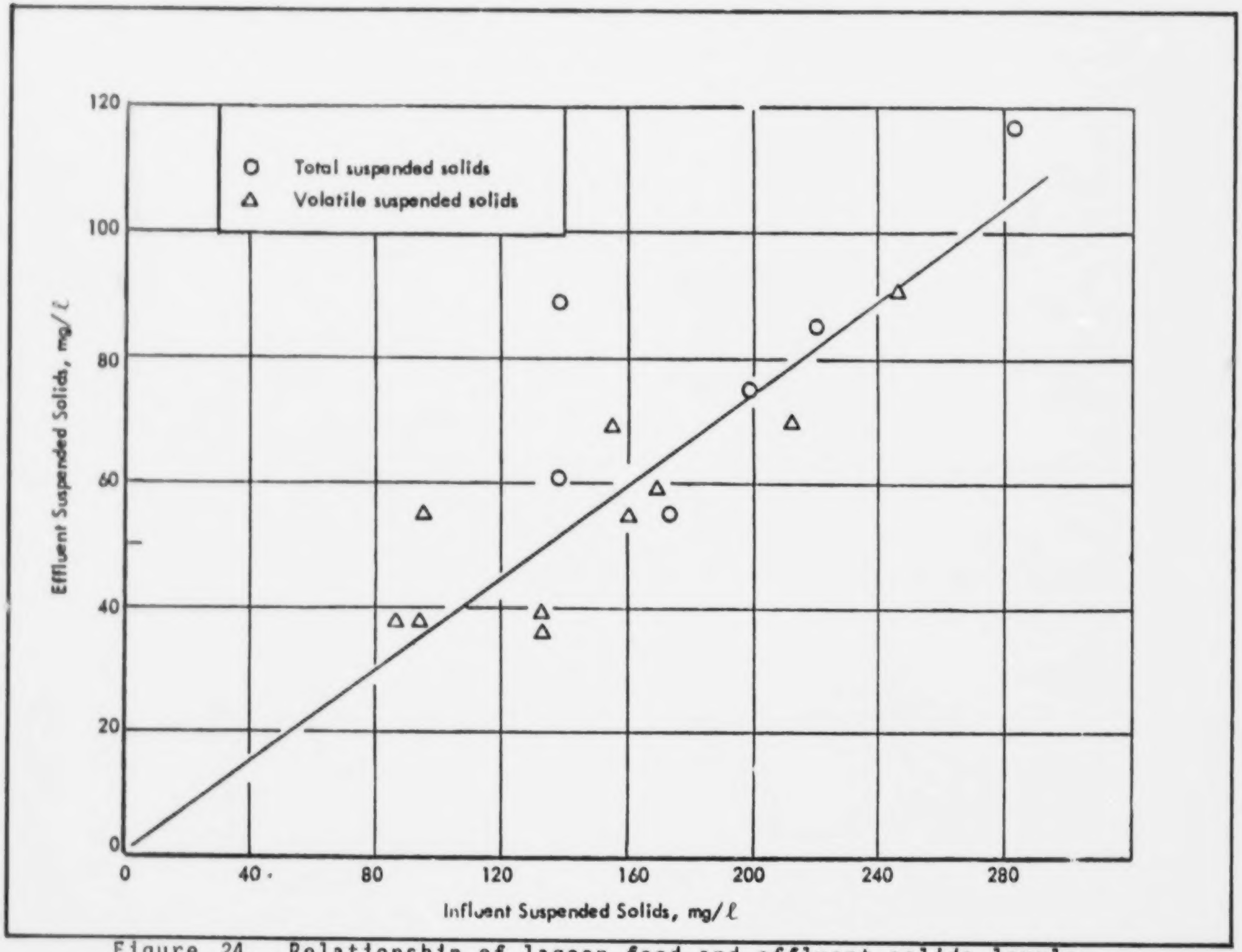


Figure 24. Relationship of lagoon feed and effluent solids levels.

suspended solids (VSS) were removed from the effluent and stored in the lagoons. At the end of this operational period, solids remaining in the lagoon system were composed of 467 kg (1,030 lb) of TSS and 39 kg (86 lb) of VSS. A material balance proved that degradation of total and volatile suspended solids amounted to 50 and 70 percent, respectively.

OPERATIONAL INFORMATION

The 40-Acre treatment facility is monitored daily at sampling stations located within the lagoon system. This enables the GCWDA operators to select a treatment scheme to best handle the incoming waste streams. For example, a wastewater with a low organic content will not require the total aeration capabilities of the aerated stabilization basins. Individual aeration units can be shut off, or a basin may be bypassed, reducing maintenance and energy costs. Table 52 shows the variety of operational modes which have been used at the facility from February 1975 to May 1977.

Sampling and monitoring stations within the lagoon system are located so that each of the four biological processes (anaerobic, limited aeration, aerated stabilization, and facultative) can be monitored. Sampling platforms are located in each of the anaerobic lagoons and in the limited aeration basin (Figure 25). Samples from the aerated stabilization basins are taken from a skiff. The facultative lagoon effluent is monitored at the outfall station.

Flow proportional composite samplers, with associated refrigeration units, are located so that samples can be drawn from influent and effluent streams and from the influent to the aerated stabilization basins (Figure 25). Grab samples are used to analyze waste in the aerated stabilization basins.

The following pages describe the parameters measured in the individual basins and the representative values thereof. The monitoring data for the facultative lagoons are included in the "Treatment Efficiency" section of this report.

Anaerobic Lagoons

The anaerobic lagoons were used to treat Influents A, B, and D until February 1976. At that time the southern anaerobic lagoon was converted to a limited aeration basin with the addition of 14 surface aerators. The two other anaerobic lagoons remained idle until October 1976, when Influent B_1 was transferred to the lagoon. Table 53 summarizes the anaerobic lagoon effluent data for 1975.

TABLE 52. GCWDA 40-ACRE OPERATIONAL MODES AS OF FEBRUARY 1975

February 1975 - March 1975

Influents A, B, and D into equalization basin (EQB) into #2 Anaerobic Basin into splitter box. Influent C enters at splitter box. Parallel flow into the Aerated Stabilization Basin (ASB) into #3 Facultative to #2 Facultative and out.

April 1975 - May 1975

Flow same as above. Parallel flow to ASB into #3 Facultative and out.

June 1975 - February 1976

Influents A, B, and D direct to #1 Anaerobic Basin to #1 ASB into #2 ASB. Influent C enters splitter box directly into #2 ASB (bypassing #1 ASB) and combined flow exists to #3 Facultative and out.

February 1976 - June 1976

Influents A, B, and D into EQB into Limited Aeration Basin (LAB) into splitter box mixing with Influent C. Parallel flow into ASB into #2. Facultative and out. Approximately 6 aerators off in #2 ASB in April and May.

July 1976 - October 1976

Flow same as above until after splitter box and then directly into #2 ASB and then to #2 Facultative and out.

November 1976 - December 1976

Influents A and D to EQB, Influent B directly to LAB, Influent B_1 directly to #1 Anaerobic on to #2 Anaerobic (no effluent). LAB effluent to splitter box mixing with Influent C and then parallel to the ASB to #2 Facultative and then out. Approximately 9 aerators off in #1 and #2 ASB.

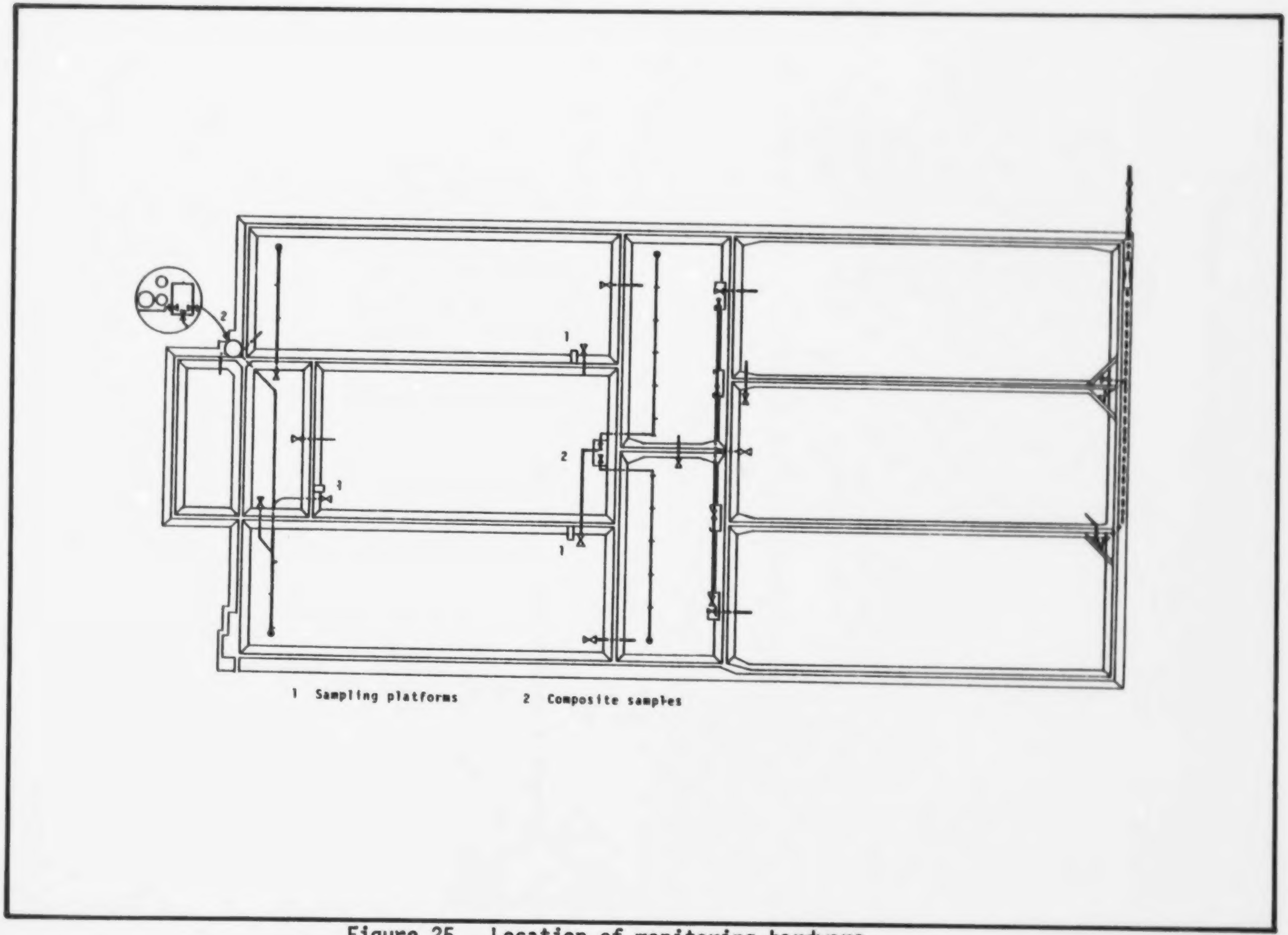

1
2
1
2
1
1
1 Sampling platforms
2 Composite samples

Figure 25. Location of monitoring hardware.

TABLE 53. 40-ACRE FACILITY: ANAEROBIC LAGOON
(1975 Data*)

Parameter	mg/ℓ	Range	kg/day	(lb/day)
TOC	295	208- 420	12,478	(27,509)
COD	971	668-1222	41,123	(90,660)
BOD	520	297- 946	22,108	(48,740)
TSS	34	19- 78	1,470	(3,241)
VSS	17	9- 37	717	(1,581)
Alkalinity	878	643-1135	36,746	(81,011)
Volatile acids	166	68- 290	7,149	(15,760)
P^{O}	17.2	2- 34	744	(1,640)
NH_3-N	30.3	18- 46	1,284	(2,831)
Sulfide	5.73	0.4- 14.7	249	(549)
SO_4	57.9	32- 112	2,395	(5,280)

pH average 9.3, range 9.0 - 9.7
Temperature average 29°C, range 21 - 35°C

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* Average of daily reports for the entire year

TABLE 54. 40-ACRE FACILITY: LIMITED AERATION BASIN EFFLUENT QUALITY (1976)

Parameter	mg/ℓ	Range	kg/day	(lb/day)
TOC	101	67- 146	3,371	(7,432)
COD	396	286- 562	14,429	(31,810)
BOD	104	63- 201	3,561	(7,851)
TSS	157	101- 277	5,479	(12,079)
VSS	127	82- 214	4,495	(9,910)
P^o	3.99	1.62- 14.82	109	(240)
NH_3-N	12.6	2.15- 20	513	(1,131)
Sulfide	0.18	0.04- 0.28	1.0	(2.0)
SO_4	67	38- 104	2,658	(5,860)
D.O.	1.7	0.9- 3.2	64	(141)
Cl^-	2265	1231-3179	81,479	(179,630)
TDS	4707	3112-5924	173,422	(382,330)
TKN	19.8	6.3- 28.7	324	(714)

pH average 7.9, range 7.6 - 8.2

TABLE 55. AERATED STABILIZATION BASINS F/M RATIOS FROM 1975-1976

Date	#1 Basin	#2 Basin	Mode of Operation
Feb 1975	0.74	0.82	Parallel
March	0.44	0.48	
April	0.84	0.64	
May	1.20	1.03	
June	1.46	0.69	Series with Influent entering #2 basin
July	5.03	1.07	
Aug	1.75	0.55	
Sept	1.22	0.46	
Oct	0.93	0.39	
Nov	0.95	0.32	
Dec	0.69	0.44	
Jan 1976	0.84	0.58	
Feb	1.15	0.65	
Mar	0.45	0.41	Parallel
April	0.50	0.39	
May	0.62	0.47	
June	0.48	0.52	
July		1.11	#2 basin only
Aug		0.80	
Sept		0.93	
Oct		0.68	
Nov	(no sampling)	0.65	Parallel
Dec	(no sampling)	0.46	

TABLE 56. 40-ACRE FACILITY: AERATED STABILIZATION BASINS (ASB) MONITORING DATA (1975)

	ASB #1				ASB #2			
Parameter	mg/ℓ	Range	kg/day	(lb/day)	mg/ℓ	Range	kg/day	(lb/day)
TOC	112	78-185	5,271	(11,621)	98	62-160	5,012	(11,050)
COD	498	390-652	24,031	(52,979)	451	388-651	21,723	(47,891)
BOD	.36	7-174	3,130	(6,900)	23	8- 81	3,275	(7,220)
TSS	222	108-321	11,294	(24,899)	231	171-341	26,080	(57,497)
VSS	176	71-263	8,963	(19,760)	170	116-245	8,677	(19,130)
SS	15.5	0.4- 69.0	1,220	(2,690)	16.9	2.2 - 81	975	(2,150)
NH_3-N	41.8	20- 82.3	2,159	(4,760)	43.4	24- 70.6	2,214	(4,881)
pO	13.0	0.32- 25	939	(2,070)	11.7	0.25- 21.8	612	(1,349)
D.O.	4.1	1.3 - 7.3	204	(450)	5.5	3.5 - 7.6	279	(615)
D.O. Uptake	6.3	2.6 - 16.3	331	(730)	3.6	1.8 - 7.6	181	(399)

pH: avg 8.1 range 7.9 - 8.3
Temperature: avg: 26 range 19-32

pH avg: 8.1 range 7.9 - 8.3
Temperature avg: 25 range 18-31

TABLE 57. 40-ACRE FACILITY: AERATED STABILIZATION BASINS (ASB) MONITORING DATA (1976)

Parameter	ASB #1				ASB #2			
	mg/ℓ	Range	kg/day	(lb/day)	mg/ℓ	Range	kg/day	(lb/day)
TOC	77.5	42.6-120.4	3,493	(7,700)	72.18	42.9- 99.6	3,311	(7,300)
COD*	192.3	156.6-255.6	8,664	(19,101)	180.9	143 -213	8,301	(18,301)
BOD	22.15	11.9- 45.9	998	(2,200)	18.4	9.9- 26.9	844	(1,861)
TSS	184.28	103 -253	8,301	(18,301)	209.6	136.9-298.7	9,616	(21,200)
VSS	151.05	74.9-229.4	6,804	(15,000)	155.2	100.9-211.4	7,121	(15,699)
SS	13.39	1.9- 23.4	603	(1,330)	13.94	4.1- 28.6	640	(1,411)
NH_3-N	19.13	4.8- 36.4	862	(1,900)	33.72	11.3- 64.6	1,547	(3,411)
P^{O}	1.00	0.21- 1.94	45	(99)	1.29	0.25- 8.6	59	(130)
D.O.	6.14	3.6- 8.0	277	(611)	5.73	5.25- 7.36	263	(580)
D.O. Uptake	4.73	1.5- 9.4	213	(470)	3.95	2.04- 5.36	181	(399)

pH avg: 8.0 range 7.7-8.5

pH avg: 8.1 range 7.9-8.4

* Five day, COD

TABLE 58. TWQB DAILY AVERAGE EFFLUENT LOADING DISCHARGE LIMITATIONS: 8/75-7/77, AND THE CORRESPONDING MONTHLY 40-ACRE EFFLUENT LOADING DISCHARGE FOR MARCH 1975-APRIL 1977

	Effluent Characteristic in kg/day (lb/day)				
	BOD_5	COD	TSS	Oil & Grease	Ammonia-N
TWQB EFFLUENT LIMITATIONS	2953 (6510)	23627 (52089)	6497 (14323)	297 (655)	2859 (6303)
August 1975	919 (2026)	16825 (37093)	3790 (8356)	40 (88)	2814 (6203)
September	610 (1345)	14076 (31032)	2161 (4764)	55 (121)	1834 (4043)
October	915 (2017)	14012 (30891)	2985 (6581)	29 (64)	2778 (6124)
November	981 (2163)	15903 (35060)	4234 (9334)	26 (57)	3397 (7489)
December	982 (2165)	14003 (30871)	3359 (7405)	41 (90)	2945 (6493)
January 1976	967 (2132)	14856 (32752)	4935 (10880)	35 (77)	1445 (3208)
February	1068 (2355)	15556 (34295)	3813 (8406)	31 (68)	1312 (2892)
March	1096 (2416)	14019 (30907)	2827 (6232)	44 (97)	2452 (5406)
April	756 (1667)	12268 (27046)	2268 (5000)	54 (119)	2047 (4513)
May	559 (1232)	9804 (21614)	1372 (3025)	76 (168)	1483 (3269)
June	497 (1096)	11432 (25203)	1823 (4019)	133 (293)	1082 (2385)
July	652 (1437)	12611 (27802)	2935 (6471)	109 (240)	1169 (2577)
August	594 (1310)	11560 (25485)	2924 (6446)	78 (172)	2106 (4643)
September	827 (1823)	11368 (25062)	2480 (5467)	89 (196)	2046 (5511)
October	939 (2070)	10827 (23869)	2620 (5776)	54 (119)	2788 (6146)
November	944 (2081)	14690 (32386)	4512 (9947)	89 (196)	2440 (5379)
December	1422 (3135)	18246 (40226)	6220 (13712)	172 (379)	2198 (4846)
January 1977	3971 (8755)	29876 (65865)	10570 (23303	159 (350)	1833 (4041)
February	1823 (4019)	18943 (41762)	6382 (14070)	106 (234)	2401 (5293)
March	856 (1887)	14398 (31742)	4496 (9912)	134 (295)	2532 (5582)
Mean	1096 (2357)	14764 (32549)	3835 (8455)	78 (172)	2156 (4753)

TABLE 59. TWQB EFFLUENT LOADING
DISCHARGE LIMITATIONS EFFECTIVE JULY 1, 1977

Effluent Characteristic	Discharge Limitations in kg/day (lb/day)	
	Daily Average	Daily Maximum
BOD_5	1,769 (3,900)	3,983 (8,781)
COD	20,639 (45,501)	31,298 (69,000)
TSS	2,722 (6,001)	5,897 (13,000)
Oil and Grease	297 (655)	593 (1,307)
Ammonia-N	594 (1,310)	1,188 (2,619)

Limited Aeration Basin

Aerators were added to one anaerobic basin to help eliminate the sulfide odors that had been a problem in the anaerobic lagoons. The aerators maintain dissolved oxygen levels in the basin between 1 and 2 mg/ℓ. Table 54 summarizes the limited aeration basin effluent data for 1976.

Aerated Stabilization Basins

Grab samples are used to analyze constituents in the aeration basins. Dissolved oxygen levels are maintained above 2 mg/ℓ. In the basins, the food-to-micoorganism (F/M) ratio averages 0.34 kg BOD/kg MLSS (0.34 lb BOD/lb MLSS) when the waste flow is split and passed in parallel through the two basins. The F/M ratios in the basins for 1975-76 are summarized in Table 55. To determine the operational status of the basins for a specific month, values from this summary are compared with the modes in Table 52. Tables 56 and 57 show the values of operational parameters for 1975 and 1976, respectively.

In addition to the waste parameters shown in Tables 56 and 57, the amounts of ammonia and phosphorus are also monitored in the plant effluent. When there are not enough nutrients in the effluent, chemical nutrients, such as NH_3 and H_3PO_4, are added. However, since Influents C and D have been included in the waste stream, nutrient addition has not been required.

TREATMENT EFFICIENCY

The first portion of this discussion will present the ability of the treatment facility to meet effluent limitations set by the Texas Water Quality Board (TWQB). The second portion will present the overall efficiency of the system in terms of wastewater constituent removal.

Effluent standards for the facility are set by the TWQB, in accordance with the NPDES program. Effluent limitations are set in loading values (kg/day) and not in concentration values (mg/ℓ). Table 58 shows the effluent loading limitations in force from August 1975 through July 1977 and the corresponding effluent loading values for August 1975 through March 1977. Table 59 shows the effluent limitations that took effect on July 1, 1977.

In certain instances, the effluent did not meet established effluent loading discharge limitations. For example, in January 1977 the limitations were exceeded by the BOD_5, COD, and ammonia-N effluent loading discharge values. An evaluation of the temporary excesses indicated that the removal capabilities of the biological system had been exceeded at this time and that specific influent loading limits would be necessary if the system is to meet regulatory requirements. However, the facility

TABLE 60. AVERAGE WASTEWATER CONSTITUENT REMOVAL EFFICIENCY - MAY 1975 THROUGH DECEMBER 1976

Wastewater Characteristic	% Reduction	Range	No. of Months for Which Data is Available
TOC	75.8	59.9- 81.7	20
COD	75.8	65.7- 78.6	20
BOD	96.3	91.5- 98.1	20
TSS	33.0	-33.8- 69.0	20
VSS	-23.5	-171.9- 42.8	20
TDS	- 4.24	-21.1- 9.9	12
P^o	70.7	35.4- 98.0	20
NH_3-N	-69.5	-241.5- 42.6	20
S^o	-128.8	-234.5--73.1	8
Phenol	10.6	-165.2- 97.3	17
Cl^-	-9.8	-34.5- 7.7	8

* Negative values indicate increase in the effluent loading over the influent loading.

is not a static system. The retention and aeration period and treatment processes are not fixed and can be varied by the operators. Consequently, although the capabilities were exceeded during a certain period, it cannot be concluded that system removal limitations were reached; loading limitations require further study.

Removal efficiency levels for various wastewater constituents are maintained by modifying the treatment schemes, for example, series vs. parallel flow in the aeration basins, and amount of aeration. These operational modes should be referred to (see Table 52) when reviewing the treatment efficiencies shown in the following tables. Table 60 summarizes the average treatment efficiencies for May 1975 through December 1976. It should be noted that in certain instances, loading data for all influent constituents are not available. Table 60, therefore, includes indications of the number of months for which data were available.

In reviewing the values in Table 60, it should be noted that removals of TOC, COD, and BOD are constant, while reductions of other constituents fluctuate widely. The main objective of biological treatment systems is the removal of oxygen-demanding materials. The absence of highly fluctuating TOC, COD, and BOD values indicates a stable and well-acclimated microbial population in the various treatment steps. In addition, the COD removal of 76 percent reflects the beneficial effects of the long retention time of the 40-Acre system. Many organic petrochemical wastewater constituents, especially complex synthetic organic compounds, are consequently recorded as COD. These organics are the principal reason why smaller scale, high-rate systems treating petrochemical wastewater show such poor TOC removal efficiencies. The long retention characteristic of the 40-Acre system allows the plant biota sufficient time to degrade the resistant-organic molecules.

The apparent increases in certain wastewater constituents are, however, somewhat misleading. For example, Influent A is not tested for NH_3-N because concentrations are quite low. However, with a high flow of the wastewater, up to 40 x 10^3 m^3/day (10.5 MGD), the loading values of even a low concentration will be significant. This premise is also applicable to the apparent increase in effluent oil and grease loading over the influent loading.

Conditions in the facultative lagoons are conducive to algal growth. Increases in the loading in the effluent, when compared to influent loading values, are due primarily to the presence of algae.

TDS and Cl^- ion concentrations are not appreciably affected by the 40-Acre system. Influent vs. effluent TDS and Cl^- loadings

TABLE 61. MAJOR ASSUMPTIONS OF THE CONSTRUCTION COST ESTIMATE

1. Earthwork slopes are two horizontal units for each vertical unit.

2. Piling is required under all major structures.

3. A Gulf Coast location is assumed.

4. All earthen basins are lined with four inches of concrete from the top of the slope to two feet below the water surface unless otherwise noted.

5. Basin interconnect piping is low-head corrugated metal drainage pipe with protective coating.

6. All costs adjusted to 1976 dollars.

TABLE 62. CONSTRUCTION COST ESTIMATE: ANAEROBIC-AERATED STABILIZATION SYSTEM

	53×10^3 m^3/Day Flow (14 MGD), 65 ha (160 ac)
Neutralization	
Structural	$ 46,200
Mixing	19,530
Reagent Storage	63,840
pH Control	25,200
Clarification	
Structural	259,560
Mechanical Equipment	123,900
Anaerobic Ponds	
Earthwork	685,650
Concrete Liner	82,530
Aerobic Basin	
Earthwork	439,950
Concrete Liner	68,880
Aeration Equipment	940,800
Electrical Support	179,550
Facultative Ponds	
Earthwork	284,550
Concrete Liner	124,110
Piping	351,540
Instrumentation	117,600
Building and Lab Equipment	107,100
Site Preparation	103,110
Land at $1,000/acre	160,000
Subtotal	$4,183,600
Construction Contingency	433,716
Construction Cost	$4,617,316

remain relatively equal or vary slightly. Effluent increases could be due to chemical reactions within the system, and decreases could be due to chemical complexes in the sludge floc.

ECONOMIC EVALUATION

The GCWDA 40-Acre facility was constructed in 1974 at a cost of $5.5 million, with financial assistance from Pollution Control Revenue Bonds. The system was designed for simplicity of operation and with few major structural components (e.g., sludge dewatering equipment) so as to save on both annual operating and maintenance costs. However, the system is land intensive, covering 160 ac. The 1976 operation and maintenance costs totaled $550,000; 60 percent was funded by Discharger the remainder by Discharger 2. Power requirements, including aeration demands, totaled $350,000; labor costs, $135,000; and other supplies, $30-40,000.

There were chemical cost savings when Influent D was added to the facility influent. Phosphoric acid and hydrochloric acid addition costs had approached 10 percent of O&M costs; the low pH (2-3) and high phosphorus content of Influent D made the addition of these acids unnecessary.

An economic comparison between activated sludge and anaerobic-aerated and stabilization-facultative systems is included in Anaerobic Treatment of Synthetic Organic Wastes, by Hovious et al. (66). Using the information in this report and referring to appropriate economic indices, construction costs (in 1976 dollars) can be projected for a system similar to 40-Acre. This system includes pH adjustment, primary clarification, anaerobic, aerated stabilization, and facultative lagoons. Table 61 lists the major assumptions of the construction cost estimate. The estimate is shown in Table 62.

In 1976, the average influent and effluent BOD_5 loadings were 26,101 kg/day (57,543 lb/day), and 860 kg/day (1,896 lb/day) respectively, for a net BOD_5 reduction of 25,241 kg/day (55,647 lb/day). The 1976 operation and maintenance costs of $550,000 plus the annual amortization of $480,000 ($5.5 million over 20 years at 6 percent) yield a total annual cost of $1,030,000. The 40-Acre system cost per kilogram BOD_5 removed is $0.11 ($10.11/ lb BOD_5).

GULF COAST WASTE DISPOSAL AUTHORITY (GCWDA)
WASHBURN TUNNEL INDUSTRIAL WASTE TREATMENT FACILITY
PASADENA, TEXAS

INTRODUCTION

The Gulf Coast Waste Disposal Authority (GCWDA) Washburn Tunnel Facility, a large high-rate activated sludge plant in Pasadena, Texas, is capable of processing about 2.1 x 10^5 m^3/day (55 MGD). The 9.7 ha (24 ac) site includes primary treatment facilities for barscreening and grit removal and primary clarification. Nutrient addition, pH control, and cooling towers are used to prepare the primary effluent for introduction to the complete-mix aeration basins which are equipped with mechanical surface aerators. Effluent from these basins is passed into one of two secondary clarifiers, where a percentage of the sludge is wasted to a filter press-incinerator installation, and the remainder is cycled back to the aeration basins. Sludge centrifuges, and a control building, control systems, and a minicomputer are also at the site. All clarification and aeration basins have concrete walls and bottoms. Two spill lagoons located at the east side of the plant are used only when extremely toxic or concentrated wastes are accidently introduced to the plant and must be diverted and reintroduced slowly to avoid system upset.

The plant treats six industrial waste streams and discharges to the Houston Ship Channel. Presently, sludge is barged to an off-site landfill but it will eventually be burned in a new incinerator.

HISTORY

GCWDA participation in industrial waste treatment was authorized under the statute creating the authority, adopted by the Texas Legislature in September 1969. The letter of agreement GCWDA signed in September 1970 with five industries was the initial step in forming the first joint waste treatment facility in the Gulf Coast area. Compatibility-treatability tests, funded by the industrial participants, were used to determine if the individual wastes could be combined in a single biological treatment plant. In November 1970, the Texas Water Quality Board approved the concept of joint treatment contingent upon proof of waste compatibility and authorized GCWDA to proceed with the project.

Contracts between GCWDA and the industries were signed in May 1973. Subsequently, \$25 million in bonds were issued; \$12-1/2 million were to go to the purchase of an existing 1.7 x 10^5 m^3/day (45 MGD) treatment plant. The contract also stipulated that, following the bond sale and plant purchase, GCWDA would become owner and operator of the facility. Under the terms of the agreement, the participating industries contracted to pay all bond amortization, maintenance and operating costs, plus a management fee to the GCWDA in the amount of \$120,000 annually.

In 1973, an expansion program was begun which would provide an additional biological train and sludge handling facility and expand the plant capacity to 2.1 x $10^5 m^3$/day (55 MGD). The total cost of the expansion, \$14 million, was financed by the remainder of the original bond issue.

LOCATION

The Washburn Tunnel Facility is located in the city of Pasadena on the east side of Houston, Texas (Figure 26). The facility is on the southern shore of the Houston Ship Channel, and the plant effluent is discharged to the channel. The Vince Bayou is to the west of the facility and the Washburn Tunnel (an automobile tunnel under the ship channel) is located to the east (Figure 27).

REGIONAL CHARACTERISTICS

Refinery and petrochemical production and storage facilities are the major industries of the area. This southeastern portion of Texas contributes 30 percent of the total U.S. petrochemical output. The ship canals and nearby Galveston Bay and Gulf of Mexico provide excellent transportation routes for raw materials and finished products. Crude oil from nearby petroleum reserves in Texas, Oklahoma, and Louisiana is easily piped or trucked into the area. The land is relatively flat, and underground pipelines are easily installed and serviced.

The advantages cited above have made industrial property adjacent to the ship canals a popular and relatively expensive commodity. Because land costs are prohibitively high, waste treatment designers have avoided sprawling, land-intensive lagoon treatment schemes. The Washburn Tunnel has a low surface-to-volume ratio typical of process schemes consisting of separate, deep basins. This has mandated the use of innovative techniques for waste temperature control prior to biological treatment.

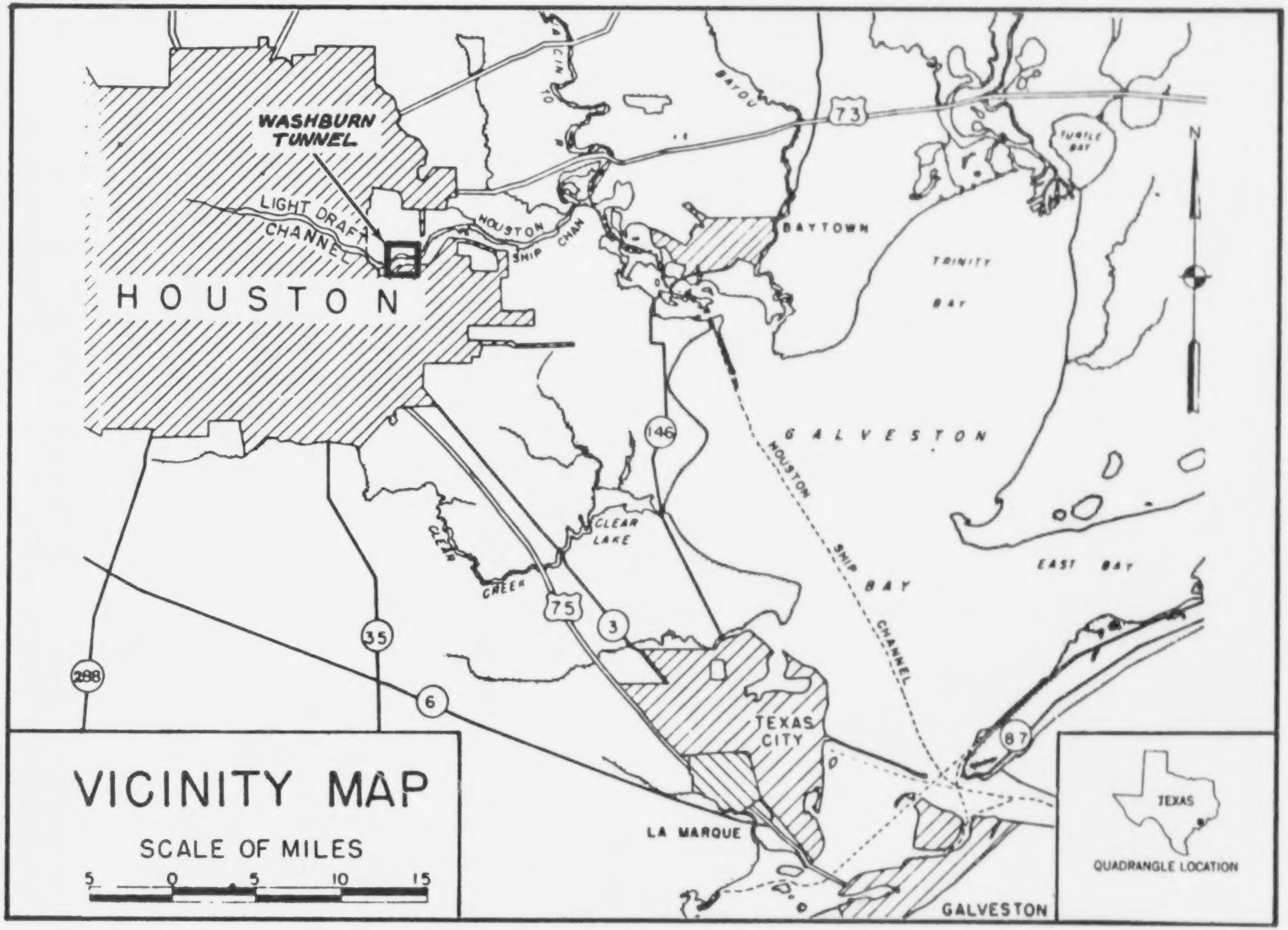

WASHBURN TUNNEL
LIGHT DRAFT CHANNEL
HOUSTON
HOUSTON SHIP CHAN
SAN JACINTO R
BAYOU
73
BAYTOWN
TURTLE BAY
TRINITY BAY
N
GALVESTON
HOUSTON SHIP BAY CHANNEL
146
CLEAR LAKE
CLEAR CREEK
EAST BAY
75
3
35
288
6
TEXAS CITY
LA MARQUE
87
GALVESTON
TEXAS
QUADRANGLE LOCATION
VICINITY MAP
SCALE OF MILES
5
0
5
10
15

Figure 26. Map of Houston. Texas and vicinity.

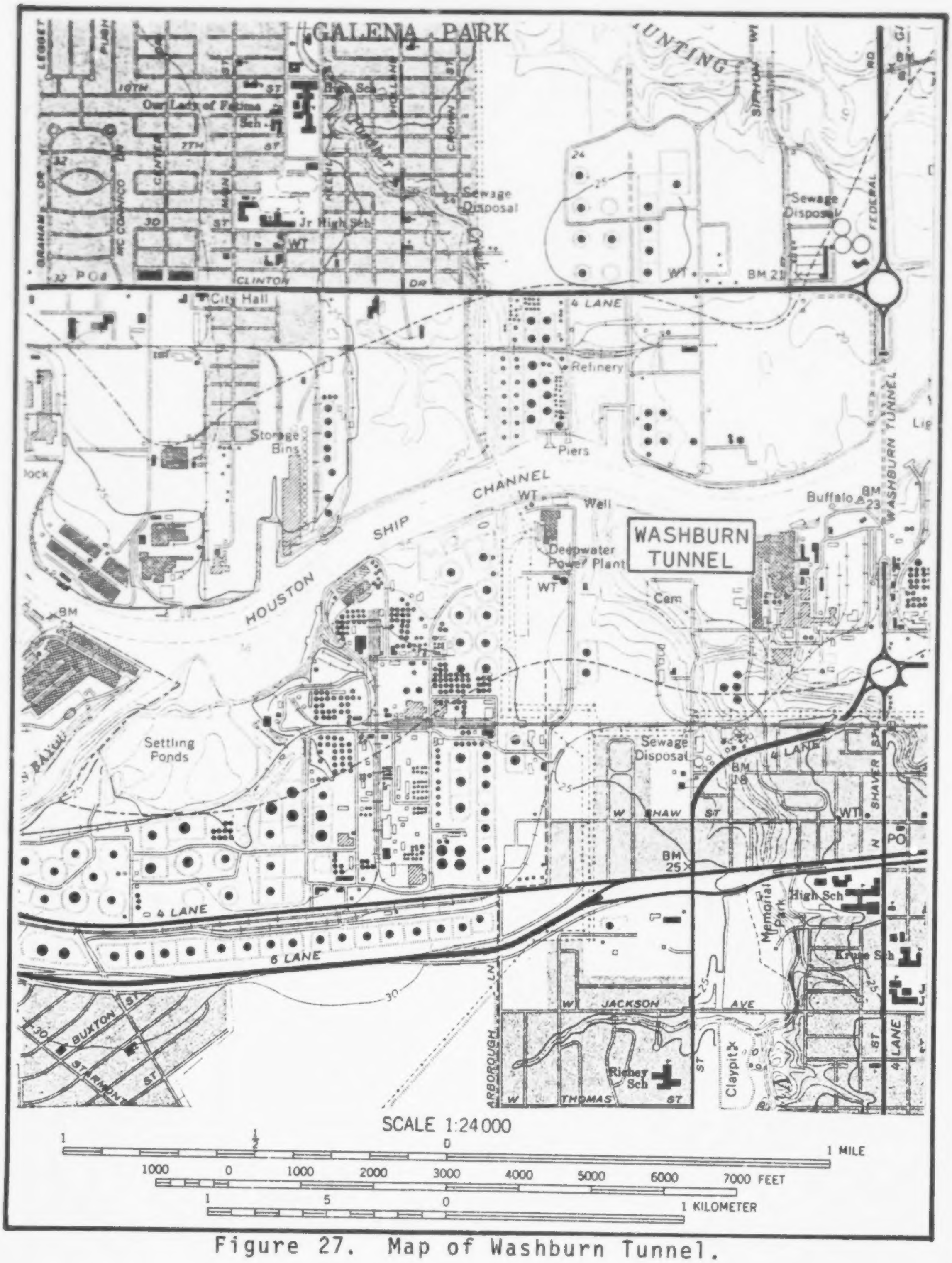

GALENA PARK
High Sch
Our Lady of Fatima Sch
Jr High Sch
Sewage Disposal
CLINTON DR
City Hall
4 LANE
Refinery
Storage Bins
Piers
HOUSTON SHIP CHANNEL
WT
Well
Deepwater Power Plant
WASHBURN TUNNEL
Cem
Buffalo
BM 23
BM 21
Settling Ponds
Sewage Disposal
W SHAW ST
BM 18
BM 25
PO
4 LANE
6 LANE
High Sch
Memorial Park
Kruse Sch
W JACKSON AVE
BUXTON ST
Richey Sch
W THOMAS ST
Claypit
SCARBOROUGH LN
SHAVER ST
FEDERAL RD
WASHBURN TUNNEL
SCALE 1:24000
1
½
0
1 MILE
1000
0
1000
2000
3000
4000
5000
6000
7000 FEET
1
5
0
1 KILOMETER

Figure 27. Map of Washburn Tunnel.

Temperatures in the Gulf Coast region of Texas are moderated by coastal winds, with summer daily maximums in the low thirties (degrees centigrade, Table 63). Rainfall is fairly evenly distributed throughout the year, and the annual rainfall exceeds average potential evapotranspiration. A large portion of the rainfall occurs within short periods of time and results in excessive runoff or local flooding. Relative humidity is highest along the coast and decreases inland. According to climatological data (113), the mean annual relative humidity at noon, Central Standard Time, varies from approximately 60 percent near the coast to around 35 percent in the West Texas desert region. Recurring weather conditions limit to 60 percent the possible total annual sunshine. Tropical cyclones occasionally pass through the Texas coastal zone; high winds and floodings, especially extreme tidal fluctuations near the coast, cause a great deal of damage. Effects of the storms in the vicinity of the Washburn Tunnel Facility are limited primarily to wind or tornado damage with occasional flooding.

WASTE IDENTIFICATION

Sources

In 1976, four industries discharged aqueous waste streams to the Washburn Tunnel Facility. One additional industry discharged both aqueous and concentrated sludge waste streams. The treatment plant influents are summarized below:

Source	Influent	Avg. Monthly Flow $10^3 m^3$/day (MGD)	Percent Total Flow	Description
Discharger 1	A	127.8 (34)	76	Paper mill wastes (black liquor)
Discharger 2	B	10.4 (2.7)	6	Primary petrochemicals; capacity for benzene, toluene, and xylene production
Discharger 3	C	2.4 (0.63)	1.5	Petrochemical products; capacity for vinyl acetate production by acetylene process
Discharger 4	D	0.4 (0.1)	.5	Petrochemical products; capacity for butadiene production (from butylenes)

TABLE 63. TEMPERATURES IN THE GULF COAST REGION OF TEXAS.(159).

LATITUDE 29° 39' N
LONGITUDE 95° 17' W
ELEVATION (ground) 50 Feet

NORMALS, MEANS, AND EXTREMES

HOUSTON, TEXAS
WILLIAM P. HOBBY AIRPORT

Month	Temperature: Normal: Daily maximum	Temperature: Normal: Daily minimum	Temperature: Normal: Monthly	Temperature: Extremes #: Record highest	Year	Temperature: Extremes #: Record lowest	Year	Normal degree days
(a)	(b)	(b)	(b)	9		9		(b)
J	63.6	43.6	53.6	83	1967+	17	1963+	384
F	65.5	46.0	55.8	87	1962	25	1963	288
M	71.7	50.8	61.3	88	1967	28	1965	192
A	78.0	59.0	68.5	93	1963	38	1962	36
M	85.7	66.2	76.0	94	1967	52	1967	0
J	91.1	72.0	81.6	100	1963	59	1964	0
J	92.1	73.8	83.0	101	1964	64	1967	0
A	92.8	73.6	83.2	106	1962	64	1967	0
S	89.1	69.3	79.2	98	1963	50	1967	0
O	82.3	60.4	71.4	96	1962	38	1964	6
N	71.1	50.5	60.8	88	1963	32	1968	183
D	65.4	45.9	55.7	82	1964	19	1963	307
YR	79.0	59.3	69.2	106	AUG. 1962	17	JAN. 1963+	1396

Month	Precipitation: Normal total	Maximum monthly	Year	Minimum monthly	Year	Maximum in 24 hrs.	Year
(a)	(b)	36		36		36	
J	3.78	10.51	1944	0.86	1952	3.66	1944
F	3.44	11.33	1959	0.09	1954	5.03	1966
M	2.67	11.42	1957	0.07	1953	5.00	1957
A	3.24	8.07	1957	0.36	1937	5.18	1966
M	4.32	13.24	1968	T	1937	6.35	1968
J	3.69	14.66	1960	0.08	1936	8.51	1960
J	4.29	12.38	1942	0.07	1962	6.34	1949
A	4.27	18.51	1945	0.38	1956+	15.65	1945
S	4.26	15.40	1958	0.14	1953	5.62	1944
O	3.77	22.31	1949	T	1952	10.25	1949
N	3.86	14.36	1946	0.18	1949	7.89	1943
D	4.36	9.80	1949	0.78	1958	6.39	1964
YR	45.95	22.31	OCT. 1949	T	OCT. 1952+	15.65	AUG. 1945

Month	Snow, Sleet: Mean total	Maximum monthly	Year	Maximum in 24 hrs.	Year
(a)	36	36		36	
J	0.2	3.1	1949	3.1	1949
F	0.2	4.4	1960	4.4	1960
M	T	1.0	1968	1.0	1968
A	0.0	0.0		0.0	
M	0.0	0.0		0.0	
J	0.0	0.0		0.0	
J	0.0	0.0		0.0	
A	0.0	0.0		0.0	
S	0.0	0.0		0.0	
O	0.0	0.0		0.0	
N	0.0	0.0		0.0	
D	T	T	1961+	T	1961+
YR	0.4	4.4	FEB. 1960	4.4	FEB. 1960

Month	Relative humidity: Mid.	6 AM	Noon	6 PM
	Standard time used: CENTRAL			
(a)	8	8	8	8
J	81	84	64	67
F	81	84	60	65
M	82	86	59	62
A	86	89	63	68
M	87	90	61	66
J	88	91	61	65
J	88	91	59	64
A	87	91	59	64
S	85	88	60	65
O	83	86	52	63
N	82	85	60	68
D	81	84	64	69
YR	84	87	60	66

Month	Wind &: Mean hourly speed	Prevailing direction	Fastest mile: Speed	Direction	Year	Pct. of possible sunshine	Mean sky cover sunrise to sunset
(a)	20	13	6	6		7	20
J	11.9	NNW	32	33	1964	47	7.0
F	12.1	SSE	40	36	1963	56	6.7
M	12.7	SSE	35	30	1968+	57	6.8
A	13.0	SSE	38	16	1966+	54	7.0
M	11.7	SSE	41	17	1968	62	6.4
J	10.7	SSE	44	17	1965	72	5.6
J	8.8	S	40	36	1964	74	5.9
A	8.4	SSE	54	34	1963	70	5.7
S	9.1	SSE	31	36	1963	66	5.6
O	9.8	ESE	35	31	1967	73	4.7
N	11.2	SSE	30	14	1963	60	5.8
D	11.3	SSE	35	31	1968+	50	6.7
YR	10.8	SSE	54	34	AUG. 1963	62	6.2

Month	Mean number of days: Sunrise to sunset: Clear	Partly cloudy	Cloudy	Precipitation .01 inch or more	Snow, Sleet 1.0 inch or more	Thunderstorms	Heavy fog	Temperatures: Max.: 90 and above	Max.: 32 and below	Min.: 32 and below	Min.: 0 and below
(a)	20	20	20	36	36	30	23	8	8	8	8
J	7	4	20	11	*	2	7	0	*	6	0
F	7	5	16	10	*	3	6	0	0	3	0
M	6	13	12	8	*	2	6	0	0	1	0
A	5	7	18	8	0	4	4	1	0	0	0
M	5	13	13	8	0	7	2	6	0	0	0
J	6	17	7	8	0	7	1	19	0	0	0
J	5	17	9	9	0	10	*	26	0	0	0
A	8	15	8	9	0	9	*	[illegible]	0	0	0
S	9	12	9	9	0	7	1	[illegible]	0	0	0
O	12	10	9	7	0	3	4	3	0	0	0
N	9	8	13	8	0	2	5	0	0	*	0
D	8	9	18	10	0	2	6	0	0	4	0
YR	87	126	152	103	*	59	42	95	*	13	0

Means and extremes in the above table are from comparable exposures for periods through the current year except as noted hereafter. Annual extremes have been exceeded at other locations as follows: Highest temperature 108 in August 1909; lowest temperature 5 in January 1940 and earlier; fastest mile of wind 84 from Northwest in March 1926.

For record August 1960 through the current year.

Note:
1 cm = 0.3937 in
$^{o}C = 5/9^{o}F - 17.77$
1 Km = 0.62137 mi

Source	Influent	Avg. Monthly Flow $10^3 m^3$/day (MGD)	Percent Total Flow	Description
Discharger 5 (Aqueous)	E	26.4 (7.0)	15.7	Petrochemical products; capacity for xylene production from reformate and toluene disproportionation
Discharger 5 (Sludge)	F	0.34 (0.09)	.3	

Source: 130.

All waste flows are piped to the treatment plant facility from outlying industrial sites.

The influents, except the aqueous influent from Discharger 5 (Influent F), enter the treatment plant at pretreatment and primary treatment stages. The wastes are screened, processed for grit, and passed through primary clarifiers before going to the aeration basins. Influent F passes primary treatment and is introduced directly to the aeration basin influent.

RAW WASTE

Characteristics

Tables 64 and 65 show the average 1976 concentrations and loadings, respectively, for constituents in each of the six identified waste streams. In compliance with the National Pollutant Discharge Elimination System (NPDES), such measurements are reported monthly to the treatment plant by each industry. In 1976, Influent A contributed 76 percent of the total annual flow, and contributed 90 and 76 percent, respectively, of the total BOD_5 and COD loading. The highest average quantities of oil and grease and phenols originated in Influent B, with average monthly loadings of 2,300.1 kg/day (5,071.7 lb/day) and 567.7 kg/day (1,251.8 lb/day), respectively. In terms of concentration, Influent B was highest in average phenol content 51.7 mg/ℓ), while Influent C was highest in average oil and grease content (556.9 mg/ℓ). Influent D had the highest concentrations of BOD_5 and COD, 1,045.5 and 15,568.3 mg/ℓ, respectively. Taking into account the percentage of total flow contributed by each waste stream, the average combined waste stream temperature is 38.2°C (100.8°F), the average pH 8.0. The average temperature for the major source (Influent A) is 39°C (102.2°F). The pH ranges from 1.8 for Influent C to 11.1 for Influent D. Acidic and caustic materials have been neutralized as a result of the

TABLE 64. 1976 SUMMARY - WASHBURN TUNNEL FACILITY: INFLUENT WASTES (mg/ℓ)

Influent	A		B		C		D		E		F	
Parameter	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
Flow (x $10^3 m^3$/day) (MGD)	127.8 (33.7)	125.5-132.0	10.4 (2.7)	8.131-12.5	2.404 (0.6)	2.1-2.7	0.93 (0.2)	.66-1.26	26.4 (7.0)	20.1-28.9	0.34 (0.09)	0.14-0.63
pH	8.2	7.3-9.2	9.0	7.7-9.6	1.8	1.5-2.0	11.1	9.8-11.9	7.0	6.6-7.2	9.5	8.7-10.3
BOD_5	367.8	298-502	400.3	275-616	89.8	48-123	1045.5	519-2086	204.4	134-205	10.8	8-15
TSS	831.3	689-1046	261.5	95-507	111.3	7-604	4205.7	2554-6760	141.0	104-169	11,721.3	6,771-19,811
COD	1179.3	995-1345	1460.6	958-2801	2300.7	987-9325	15,568.3	4,446-43,904	570.0	387-636	1092.5	636-1617
Color	479.0	417-585	215.0	142-385	5575	1625-9525	520.0	--	125.0	--	40.0	--
NH_3-N	1.61	0.27-3.66	71.1	27-120	12.3	6.6-29.7	18.3	2.8-27.9	10.6	4-15	--	--
TOC	201.8	166-240	150.2	120-177	288.9	219-499	1386.6	935-2146	180.2	119-214	470.2	243-1063
CN^-	.1	--	0.6	0.11-1.27	--	--	--	--	0.3	--	0.2	--
F^-	.4	0.23-0.84	19.0	6.6-38.9	1.1	.8-2.12	0.7	0.5-0.8	0.6	0.47-0.77	1.7	1.13-2
S^{-2}	1.7	0.18-5.47	16.6	0.46-124	.04	--	--	--	1.0	--	1.0	--
Cr	.02	.01-.04	1.3	.34-5.69	--	--	1.6	0.4-4.3	0.5	0.2 0.7	0.1	--

TABLE 64 (continued)

Influent Parameter	A Average	 Range	B Average	 Range	C Average	 Range	D Average	 Range	E Average	 Range	F Average	 Range
O&G	7.7	1.8-26.1	217.6	61-447	556.9	311-1704	--	--	66.3	54-80.5	6.8	4-12
Phenols	1.8	0.43-7.87	51.7	25-97	2.5	0.02-28.23	--	--	0.7	0.05-2.81	0.05	--
NH_3-N	3.3	--	--	--	--	--	--	--	--	--	--	--
TKN	1.5	--	--	--	--	--	--	--	22.0	--	16.5	--
TDS	1550	--	--	--	--	--	--	--	1335.8	1100-1633	404.3	215.992
TP	0.9	--	0.7	0.5-0.8	0.1	--	--	--	0.3	--	1.7	--

TABLE 65. 1976 SUMMARY - WASHBURN TUNNEL FACILITY: INFLUENT WASTES kg/day (lb/day)

Influent	A		B		C		D		E		F	
Parameter	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
Flow (x$10^3 m^3$/day) MGD	127.818 (33.7)	125.498- 131.959	10.391 (2.7)	8.131- 12.469	2.404 (0.6)	2.108- 2.741	.931 (0.3)	.662- 1.264	26.35 (6.9)	20.14- 28.88	0.341 (0.09)	0.144- 0.625
pH	8.2	7.3- 9.2	9.0	7.7- 9.6	1.8	1.5- 2.0	11.1	9.8- 11.9	7.0	6.6- 7.2	9.5	8.7- 10.3
Temp.	39°C	35.5- 41.1°C	42.2°C	32.7- 48.9°C	41.6°C	36.1- 47.2°C	32°C	28.3- 39.4°C	32.6°C	27.2- 37.7°C	48°C	37.2- 62.8°C
BOD_5	47310.7 (104084)	38031- 63216	4071 (8964)	3026- 5711	210.9 (464)	78.5- 297	898.6 (1977)	479- 1511	0.862 (1.9)	3584- 6391	3.67 (8.07)	1.41- 7.26
TSS	105904.0 (232989)	87938- 134413	2808.8 (6179.4)	1050- 5621	213.4 (469.5)	16.3- 917	3736.2 (8220)	2317- 5985	3821 (8406)	2079- 4850	3971.6 (8737.5)	1046- 6831
COD	150861.1 (331894)	125554- 167932	15092.2 (33202.)	8970- 26252	4655.2 (10241.4)	2113- 10961	13023.8 (28652.4)	3592- 26685	15119.7 (33263.3)	10324- 19204	342 (752.4)	126- 539
Color	61274.9 (134805)	53751- 73391	2258.1 (4967.8)	1279- 3696	10738.3 (23624.3)	3646- 17830	--	--	--	--	--	--
NH_3-N	201.1 (442.4)	34- 452	734.3 (1615.5)	332- 1384	26.1 (57.4)	12- 53	19.3 (42.5)	2.7- 38	276.8 (609)	94- 386	0.54 (1.19)	0.45- 1.54
TOC	25835.4 (56837.9)	21,734- 31030	1574.8 (3464.6)	1255- 2087	673.4 (1481.5)	506- 950	1164.3 (2561.5)	893- 1899	4878.2 (10732)	3412- 5935	143.9 (316.6)	47- 334
CN^-	<12.7 (<27.7)	--	6.0 (13.2)	0.86- 15	<.23 (<.51)	--	--	--	N.D.	--	N.D.	--
F^-	58.6 (128.9)	29- 111	195.9 (431)	63- 424	2.49 (5.48)	1.4- 4.1	0.59 (1.3)	0.41- 0.91	15.5 (34)	9.5- 20	0.54 (1.19)	0.23- 0.91

TABLE 65 (continued)

Influent	A		B		C		D		E		F	
Parameter	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
	(MGD)		(MGD)		(MGD)		(MGD)		(MGD)		(MGD)	
S^{-2}	201.2 (442.6)	24- 687	193.4 (425.5)	3.6- 1574	<0.091 (<0.20)	--	--	--	1.45 (3.2)	--	N.D.	--
Cr	2.31 (5.08)	1.22- 5.4	11.7 (25.7)	3.2- 45	--	--	1.32 (2.9)	0.32- 3.8	12.1 (26.6)	3.2- 19	N.D.	--
O&G	957.1 (2105.6)	56- 3350	2300.1 (5060.2)	535- 4326	982.4 (2161.3)	135- 1443	--	--	1787.0 (3931)	1140- 2346	1.91 (4.2)	1.36- 2.27
Phenols	236.2 (519.6)	56- 1046	567.7 (1248.9)	200- 973	5.7 (12.5)	0.045- 64	--	--	14.2 (31.2)	1.36- 53	N.D.	--
NO_3-N	414.1 (911)	--	--	--	--	--	--	--	N.D.	--	N.D.	--
TKN	183.3 (403)	--	--	--	--	--	--	--	--	--	--	--
TDS	19459.1 (42810)	--	--	--	--	--	--	--	36053.9 (79319)	28436- 52238	147.6 (324.7)	45- 368
TP	115.7 (254.5)	--	9.3 (20.5)	--	0.23 (0.51)	--	27 (59.4)	--	--	--	N.D.	--

combining of waste streams with extreme pH; the resultant pH is in the acceptable range of biological waste treatment.

In many instances, NO_3-N and TKN were not monitored or reported. However, for the constituents reported, the ratio of biologically oxidizable carbon (BOD_5 x 0.375): nitrogen: total phosphorus is approximately 19,685.15 kg/day (43,405.8 lb/day): 1,672.24 kg/day (3,687.3 lb/day): 152.2 kg/day (335.6 lb/day), or approximately 100:8.5:0.8. The percentage of nutrients is somewhat low in relation to the calculated biodegradable carbon content, which may indicate that some nutrients must be applied to the waste prior to biological treatment.

The ranges for cyanide, fluoride, sulfides, and chromium indicate that these materials are highly variable in the waste streams. Cyanide and fluoride are not present in levels which could significantly impact biological populations in either the treatment facility or receiving waters. Influent B had the highest sulfide content, 16.6 up to 124 mg/ℓ. Chromium, which was also present in some wastes, could be a problem if not removed prior to discharge.

The combined waste flow is also monitored by the Gulf Coast Waste Disposal Authority at the influent points of the Washburn Tunnel Facility. These data are filed monthly in compliance with the NPDES Discharge Permit requirements. Table 66 lists the average waste constituent concentrations for 1976, as derived from the monthly reports. For comparison, the constituents in the waste streams shown in Table 64 have been used to estimate concentrations in the combined waste stream (correcting for percent of total flow) and are also shown in Table 66. Average waste loadings for 1976 have been calculated and are presented in Table 67; total waste stream loadings from Table 65 are shown for comparison. Differences between the average influent measurements and the values derived from the individual waste streams are probably due to error; any significant difference due to other causes is probably masked by random variation.

The values for the influent/effluent report are taken at the sampling station where the wastes are combined. As indicated previously, Influents A, C, D, and F are passed through a bar screen, grit chamber, and primary clarifiers before being combined with the aqueous Influents B and E. Primary screening and sedimentation result in the removal of settleable suspended and some colloidal materials, while relatively little of the dissolved organic or inorganic compounds are affected. It is suggested that the total suspended solids (TSS) and, to a lesser extent, the total organic carbon (TOC) would be slightly reduced at the influent sampling station.

TABLE 66. 1976 INFLUENT SUMMARY - WASHBURN TUNNEL (mg/ℓ)

	Average from Influent/ Effluent Report	Sum of Individual Flows (Table 52)**	n.r.*
Flow x 10^3 m^3/day	169.832	168.27	
pH	(not reported)	8.0	
BOD	338	342	
COD	1,199.	1,189	
TSS	704	727	
O&G	31.6	37.7	(1)
Phenol	3.9	5.0	(1)
Sulfide	1.3	2.3	(1)
CN^-	0.14	0.19	(2)
Mercury	.0027	--	(6)
TOC	184	203	
Chromium	0.19	0.17	(1)
Color	482	483	
NH_3-N	7.8	7.4	(1)
Fluoride	1.5	1.6	
TKN	(monthly average not available)	4.6	
NO_3-N	(monthly average not available)	2.6	
Total-P	(monthly average not available)	0.81	

*n.r. = number of waste streams (out of 6 total) for which the monthly average level of the constituent was not reported.

**Corrected for percent of total flow.

TABLE 67. 1976 INFLUENT SUMMARY - WASHBURN TUNNEL kg/day (lb/day)

	From influent/effluent report		Sum of individual flows (Table 65)		
Flow	1.7 x $10^5 m^3$/day (45 MGD)		1.7 x $10^5 m^3$/day (45 MGD)		(1) (n.r.)*
pH			8.0	(18)	
BOD	57,173	(126,066)	52,494	(115,749)	
COD	202,344	(53,419)	199,094	(439,002)	
TSS	119,077	(262,565)	119,958	(264,507)	
O&G	5,315	(1,403)	6,029	(1,592)	(1)
Phenol	663	(175)	824	(182)	(1)
Sulfide	203	(54)	396	(87)	(1)
CN^-	24	(6.3)	<12.7	(28)	(1)
Mercury	<.20	(<0.05)	--		(6)
TOC	31,254	(8,251)	34,270	(75,565)	
Chromium	27.4	(7.2)	27.4	(60.4)	(1)
Color	81,702	(21,569)	74,271	(163,768)	(3)
NH_3-N	1,329	(351)	1,258	(2,774)	
Fluoride	253	(67)	274	(604)	
TKN	(monthly average not available)		183.3	(404)	
NO_3-N	(monthly average not available)		414.1	(913.1)	
Total P	(monthly average not available)		152.2	(335.6)	

*n.r. = number of wastestreams monthly (out of 6 total) for which the average level of the constituent was not reported.

Effluent limitations are specifically established for the Washburn Tunnel Facility in the NPDES permit. Under the permit, the Gulf Coast Waste Disposal Authority was authorized by the state of Texas to discharge the wastes originating from specified sources to the Houston Ship Channel after a required level of treatment is achieved. Table 68 shows the permissible loading rates for various constituents in the Washburn Tunnel effluent as specified in the NPDES permit effective through June 1977. Limitations are expressed both as permissible monthly averages and maximum permissible loadings per day for any one day of the month.

Waste parameters discussed so far are those for which the facility has reported monthly averages, i.e., more than one measurement per month is made. However, as indicated, there are a number of constituents, particularly metals, that are measured once a month and reported as maximum loadings or concentrations. Averages and ranges of these monthly maximums for 1976 are shown in Table 69. Comparison of the average constituent levels in the plant effluent with the standards specified in the NPDES gives an indication of the required treatment efficiency or percent removal that must be accomplished by the Washburn Tunnel Facility. Results of this comparison are shown in Table 70. Of the parameters measured, BOD, COD, TSS, oil and grease, sulfides, cyanide, zinc, and titanium require some degree of removal to meet permit requirements. Cadmium ranged in excess of the permissible maximum only one month in the year. The rates at which other compounds, including arsenic, barium, boron, cobalt, copper, lead, manganese, molybdenum, nickel, selenium, and silver were found to be released indicated no substantial reduction required before discharge to the Houston Ship Channel.

Amenability to Biological Treatment

The following characteristics of the raw influent waste could adversely affect biological treatment:

- Elevated temperatures
- Presence of oil and grease and phenolic compounds
- High COD relative to BOD
- Presence of certain metal or nonmetal inorganic toxins
- Individual flows from sources demonstrating a potential for large pH fluctuations
- Limited amount of nitrogen and phosphorous compounds relative to the potential carbonaceous biological oxygen demand.

Process and cooling wastewaters from both petrochemical and paper production plants arrive at the Washburn Facility with a combined influent temperature between 35° and 41°C. During

TABLE 68. NPDES EFFLUENT LIMITATIONS FOR THE WASHBURN TUNNEL FACILITY - (EFFECTIVE TO

kg/day (lb/day) June 30, 1977

Parameter	Monthly Average		Permit Limit	
Temperature $^{\circ}$C	--		46°C	
pH	--		9.0	
BOD	6,736	(14,820)	13,472	(29,640)
COD	68,714	(151,171)	137,400	(302,280)
TSS	15,382	(33,840)	30,764	(67,681)
O&G	2,230	(4,906)	4,460	(9,812)
Phenol	871	(1,916)	1,742	(3,832)
Sulfide	49.5	(109)	98.9	(218)
Cyanide	15.3	(34)	30.66	(67.5)
Mercury	.497	(1.1)	.493	(1.09)
Total Cr	84.5	(186)	178.0	(392)
NH$_3$-N	1,668	(3,670)	3,337	(7,341)
Fluoride	389	(856)	777.5	(1,711)
Zinc	56.3	(124)	112.7	(248)
Titanium	997	(2,193)	1,995	(4,389)
NO$_3$-N	7,843	(17,255)	15,686	(34,509)
TKN	4,735	(10,417)	9,334	(20,534)
TDS	505,170	(1,111,374)	1,010,339	(2,222,746)
Total P	302	(664)	1,510	(3,322)
Aluminum	2,868	(6,310)	5,736	(12,619)
Arsenic	28.2	(62.04)	56.31	(123.9)
Barium	712	(1,566)	1,423	(3,131)
Boron	117.8	(259)	235.7	(519)
Cobalt	68	(150)	136	(299)
Copper	35.6	(78.3)	71.1	(156.4)
Iron	1,163.3	(2,559.3)	2,326.7	(5,118.7)
Lead	33.9	(75)	67.8	(149)
Manganese	141.9	(312)	283.8	(624)
Molybdenum	39.34	(87)	78.7	(173)
Nickel	39.6	(87)	79.2	(174)
Selenium	4.08	(9)	8.156	(18)
Silver	2.20	(4.84)	4.4	(9.7)
Cadmium	2.49	(5.5)	4.971	(10.9)

TABLE 69. WASHBURN TUNNEL FACILITY: AVERAGES OF REPORTED MONTHLY MAXIMUMS - 1976 INFLUENTS (mg/ℓ)

Parameter	Average	Range
Zinc	0.46	.34 - .65
Titanium	14.3	7.0 - 23.7
NO_3-N	4.0	<0.1 - 8.8
TKN	16.8	6.1 - 52.2
TDS	1855	1085 - 2435
Total P	1.2	0.26 - 2.25
Aluminum	15	6 - 29
Arsenic	<.003	-
Barium	.29	0.1 - 1.1
Boron	<1.0	-
Cobalt	.03	.01 - .04
Copper	.15	.03 - .26
Iron	5.02	4.18 - 6.80
Lead	.07	.01 - .15
Manganese	.77	.15 - 1.05
Molybdenum	<0.1	-
Nickel	.09	.01 - .18
Selenium	< .01	-
Silver	< .01	-
Cadmium	< .01	-
(Chromium)	0.35	.18 - 1.16
(Mercury)	0.002	0.001- 0.005
	kg/day (lb/day)	
Zinc	78.4 (172.9)	53.5 - 111
Titanium	2,446 (5,393)	1.108 - 3,837
NO_3-N	638 (1,407)	16.3 - 2,566
TKN	2,785 (6,141)	987 - 8,921
TDS	315,496(695,669)	186,710 - 384,639
Total P	207 (456)	42 - 89
Aluminum	2,540 (5,601)	995 - 4,817
Arsenic	1.77 (3.90)	<0.163- 2.16
Barium	48.1 (106.1)	16.3 - 174
Boron	50.8 (112)	26.2 - 89.4
Cobalt	4.2 (9.3)	1.36 - 6.8
Copper	24.9 (54.9)	12.7 - 44.5
Iron	858 (1,892)	510.7 - 1,101
Lead	11.7 (25.8)	<1.63 - 39.0
Manganese	132 (291)	24.5 - 193
Molybdenum	4.3 (9.5)	3.27 - 4.98
Nickel	15.9 (35.1)	1.63 - 32.7
Selenium	0.36 (0.8)	<0.159- .816
Silver	2.0 (4.4)	<0.186- 3.6
Cadmium	2.3 (5.1)	<0.163- 5.4

TABLE 70. REQUIRED LEVELS OF TREATMENT TO MEET 1976 NPDES PERMIT EFFLUENT LIMITATIONS - WASHBURN TUNNEL FACILITY

Parameter	NPDES Permit Limit-Monthly Avg. (kg/day) (effluent)	1976 Avg. Monthly Loading (kg/day) (influent)*	% Removal Required	NPDES Permit Max. Limit for any 1 day (kg/day) (effluent)	1976 Reported Maximum Loading (kg/day) (influent)	Approximate % Removal Required/Comments
BOD	6,736	57,173	88	13,472	152,887	91
COD	68,719	202,344	66	137,439	457,172	70
TSS	15,382	·119,077	87	30,764	348,618	91
O&G	2,230	5,315	58	4,460	27,495	84
Phenol	871	663	None	1,742	4,077	57
Sulfide	49.4	203	76	98.9	3,142	97
Cyanide	15.3	24.5	37	30.7	103.4	70
Mercury	497	<.204	None	0.993	0.830	None
Total Cr	84.5	27.4	None	178	186	
NH_3-N	1,668	1,329	None	3,337	17,380	
Fluoride	389	253	None	778	735	None
Zinc	56.3	78.4	28	113	111	None
Titanium	997	2,446	59	1,995	3,841	48
NO_3-N	7,843	638	None	15,686	2,566	None
TKN	4,735	2,786	None	9,334	8,921	None
TDS	505,170	315,496	None	1,010,340	389,639	None
Total-P	302	208	None	1,511	361	None
Aluminum	2,868	2,540	None	5,736	4,817	None
Arsenic	28.2	1.77	None	56.31	2.16	None
Barium	712	48.1	None	1,423	174	None
Boron	117.8	50.8	None	235.7	84.4	None
Cobalt	68	4.17	None	136	6.8	None
Copper	35.6	24.9	None	71.1	44.5	None
Iron	1,163.3	858	None	2,326.7	1,101	None
Lead	33.9	11.7	None	67.8	39.0	None
Manganese	141.9	132.4	None	283.80	193	None
Molybdenum	39.34	4.31	None	78.68	4.98	None
Nickel	39.6	15.9	None	79.2	32.7	None
Selenium	4.08	3.08	None	8.16	.816	None
Silver	2.20	1.95	None	4.41	3.63	None
Cadmium	2.49	2.27	None	4.97	5.44	8.6

* Averages for parameters in bottom half of table are based on the reported maximums; derived from one sampling per month. Averages for parameters in upper half are based on the reported monthly averages derived from multiple samples each month.

the summer, the waste stream temperature may remain above 40°C and may severely impact the biological population in the plant bioreactor. Thermophilic bacteria may proliferate under such conditions, but their instability and the occasional poor settling characteristics of the resultant floc make their presence undesirable. The time required for acclimation of mixed biological cultures at high temperatures (above 40°C) has been observed experimentally to be on the order of months (16). A temperature control system must, therefore, be provided for maintaining the wastes below this temperature if biological treatment is to be applied effectively.

Oil and grease in wastewaters may be difficult to degrade biologically in comparison with other carbonaceous materials. Volatile organic constituents or metal-bearing compounds associated with oils may also act as metabolic inhibitors or destroy cell membranes. In higher concentrations, oil and grease will form scums or slicks in treatment plant units. This phenomenon can result in reduced oxygen transfer to the aqueous waste and reduced surface area of the oily fraction for biological attack. Spill ponds must, therefore, be provided for diverting high TOC wastes suspected of being rich in oil and grease. The hydrophobic nature of oil and grease means that continuous dispersion forces must be present in the bioreactor if these materials are to be adequately degraded.

Research has shown that biological treatment of phenolic wastewaters has been successful at concentrations under 500 mg/ℓ (137). Biological techniques have reduced phenol concentrations in wastewaters at 150 to 250 mg/ℓ by 97 percent. Below a 150 mg/ℓ concentration, biological removal is often complete. It must be noted, however, that biological treatment plants are vulnerable to sudden increases in phenol loading rate. Influent wastes at the Washburn Tunnel Facility demonstrated a maximum phenol concentration of 24.8 mg/ℓ during 1976. This concentration is well below the threshold concentrations for successful biological treatment.

The organic content of the Washburn Tunnel Facility influent is low when compared with typical organic chemical waste streams. The following 1976 averages were calculated:

Parameter	Average level in influent during 1976 (mg/ℓ)
BOD_5	338
COD	1,199
TOC	184

COD concentration is approximately 3.5 times that of BOD and is indicative of the fraction of dichromateoxidizable materials amenable to biological degradation (46). The ratio for the Washburn Tunnel Facility indicates that a substantial portion of the organic wastes is not readily amenable. The ratio for other chemical industry wastes is usually around 3.0 to 6.0.

It would appear from the high ratio of COD to TOC that a portion of the COD is attributable to inorganic oxidation. Sulfides, sulfites, thiosulfates, nitrates, or ferrous iron may also be responsible for some of the COD reported in the influent.

The stability of organic carbon and oxygen demand parameters is often taken to be an indicator of the amenability of waste to biological treatment. Figures 28 and 29 show the variations in the concentrations and loadings of these parameters in the influent wastes during 1976. The range of reported monthly averages and the lowest and highest reported monthly maximum for any one sample are as follows:

Parameter	Range of the monthly averages (mg/ℓ)	Lowest reported monthly minimum (mg/ℓ)	Highest reported monthly maximum (mg/ℓ)
BOD_5	265-453	147	854
COD	1,040-1,306	577	2,717
TOC	165-219	64	430

Reported monthly maximums are relatively low compared to typical organic industrial wastes and cannot be considered "shock" loadings. The large fluctuations in COD shown in Figures 28 and 29 are probably due to the highly variable organic nature of one or more of the contributing waste streams. This can be caused by intermittent discharges from batch process areas and points out the need for spill ponds and equalization facilities.

The complex nature of industrial wastes or sewage makes an estimate of metal toxicity difficult. Toxicity must be defined in terms of the method of biological treatment, any pretreatment for metal removal, the nature of microbial populations in the bioreactor, and operational parameters such as rate of mixing and sludge age. Raw waste flows may contain chemical compounds which can form complexes with metals and reduce their toxicity. Waste streams may also contain other cations that may have synergistic or antagonistic effects with heavy metals. Unless the types of reactive organic and inorganic constituents in the wastes are known, it is difficult to gain insight into the toxic behavior of specific metals (124).

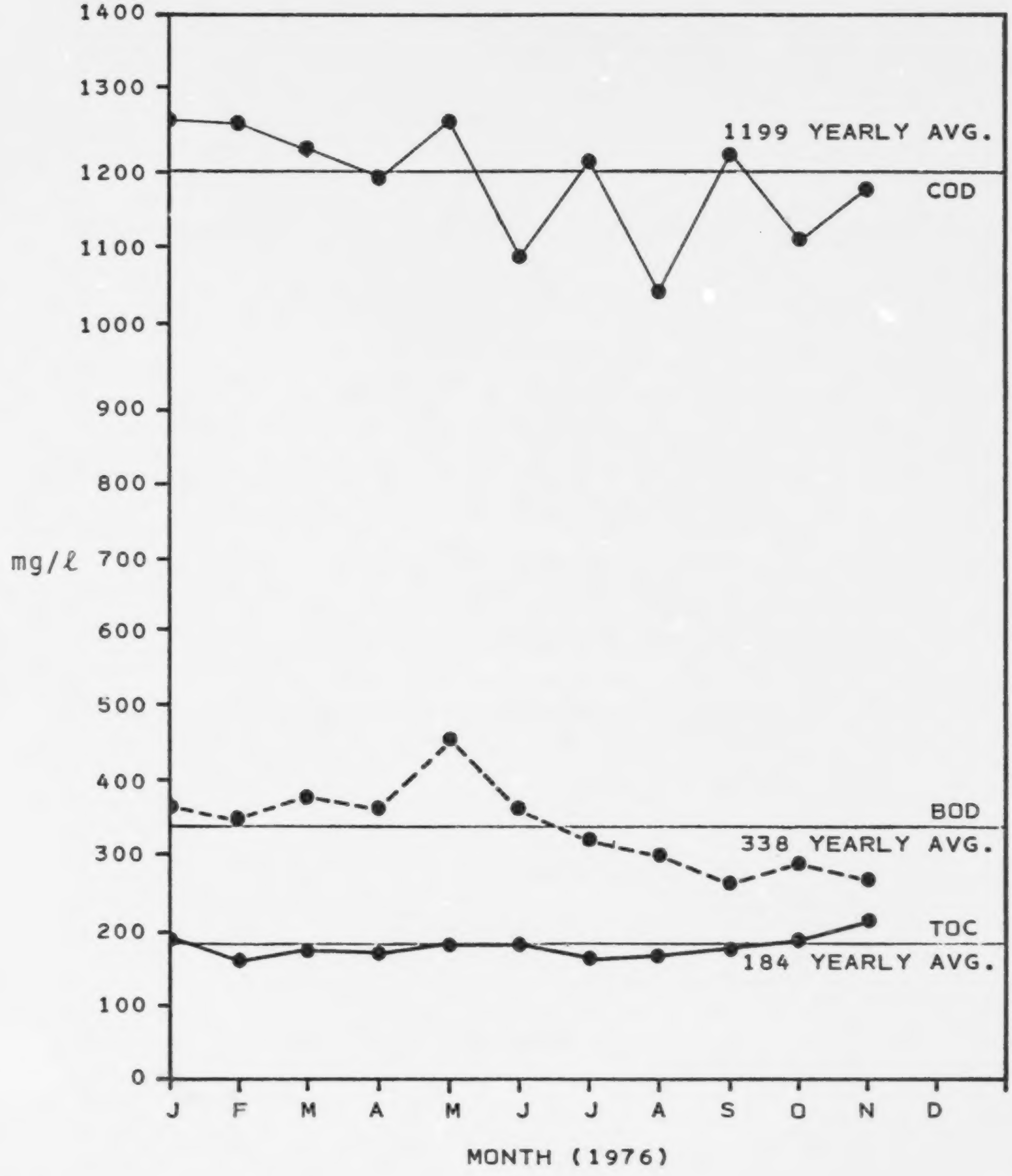


Figure 28. Washburn Tunnel Facility influent concentrations (ppm) monthly influent/effluent reports - 1976.

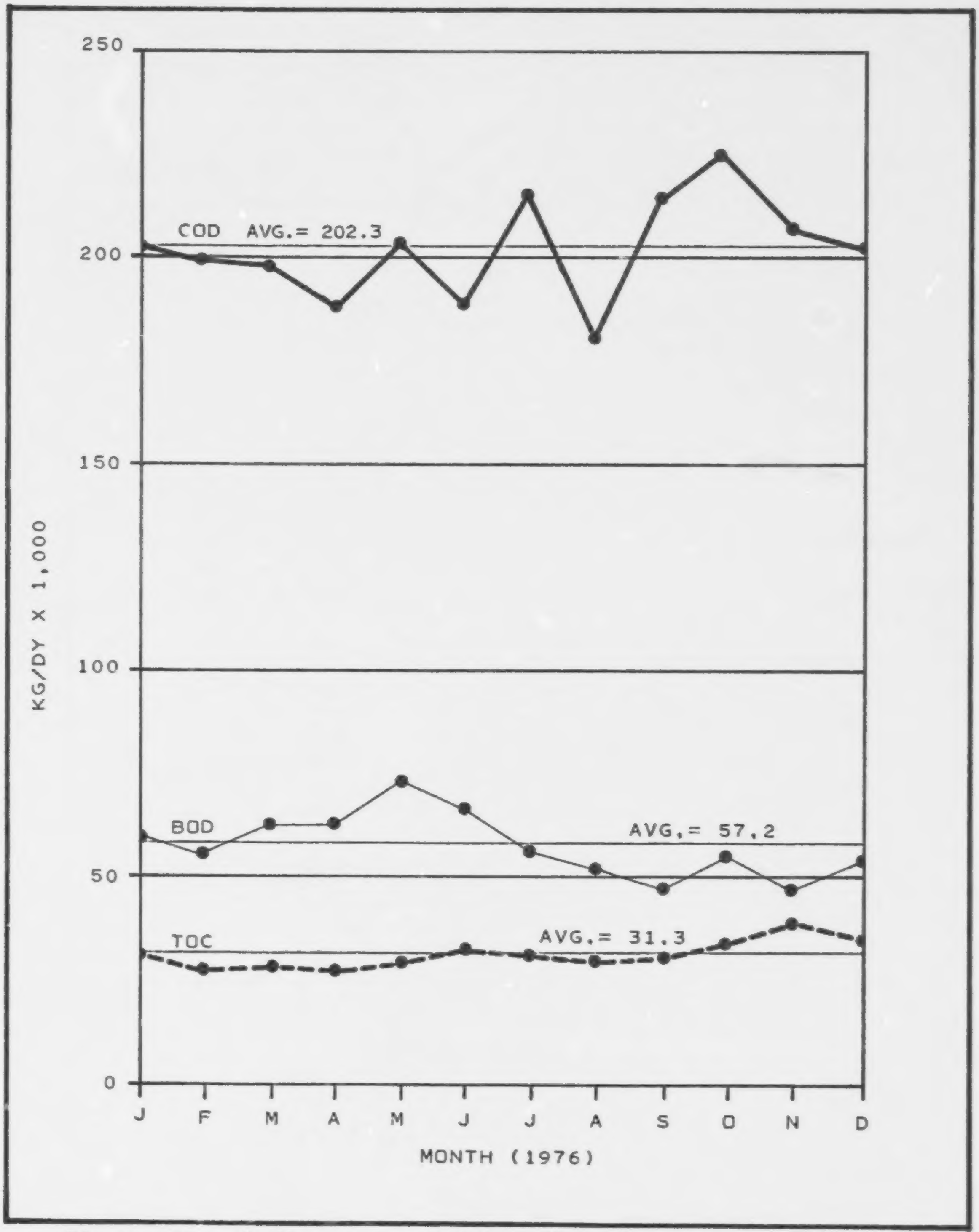


Figure 29. Influent to Washburn Tunnel treatment plant. (Avg. 1976 flow= 169.9 x $10^3 m^3$/day)

The average of the reported monthly maximum heavy metal concentrations in the influent waste is included in Table 69. The maximum level of chromium was 1.16 mg/ℓ. Studies of the impact of chromium upon activated sludge systems show that a concentration of 50 mg/ℓ is required to affect BOD removal efficiency (73). Copper is also present in innocuous concentrations (1976 maximum = 0.26 mg/ℓ). It would probably require a dose an order of magnitude more concentrated before biological treatment efficiencies were impaired. Studies on the effect of zinc on the efficiency of biological processes in removing organic matter showed that up to 10 mg/ℓ zinc in plant influent has no discernable correlation with COD or BOD levels in the final effluent (73). The maximum zinc concentration reported at the Washburn Tunnel Facility in 1976 was 0.65 mg/ℓ. Nickel is also present in the waste in concentrations well below those that have been shown to be deleterious to activated sludge plant efficiency.

Nonmetal materials present in the influent waste in trace quantities are arsenic, boron, selenium, cyanide, and various organic and inorganic sulfide compounds. Of these, arsenic, cyanide, and the sulfides can be inhibitory to microbiological degradation of organic substrates. A summary of the concentrations of these constituents in the Washburn Tunnel Facility waste influent follows:

Constituent	Avg. of reported monthly maximums (1976)* (mg/ℓ)	Highest reported 1976 monthly maximum in (mg/ℓ)
Arsenic	<.003	--
Cyanide	0.32	0.57
Sulfides	4.81	18.24

---

*Arsenic: 1 sample per month
Cyanide and sulfides: 13 samples per month.

Arsenic is a recognized biocide and may be converted to highly toxic methyl derivatives by bacteria. However, at a concentration of less than 3 μg/ℓ, it is doubtful whether the traces of arsenic in the Washburn Tunnel Facility influent have any inhibitory effect upon either biological processes at the plant or the receiving environment.

The average of the monthly maximums for cyanide in 1976 indicate that this compound is present in "borderline" concentrations where inhibition of biodegradation is questionable. In quantities above 0.5 mg/ℓ, cyanide may appreciably inhibit both nitrification and microbial respiration. Moreover, activated sludge has shown a capability to metabolize cyanide. Cyanide present in the concentrations detected in the Washburn Tunnel Facility should not be a problem to biological processes, if the bioreactor is completely mixed and receives sufficient aeration. The reported sulfide levels may also be reduced by oxidative processes in the treatment scheme.

Although the pH of individual waste sources, as shown in Table 64, ranged between 1.8 and 11.1, in 1976 the yearly average for the combined flow was 8.0. The waste pH is stabilized because the largest waste source (76 percent of the total flow) has an average pH of 8.2. The remaining industrial flows tend to neutralize one another upon mixing. However, under certain conditions, it is possible that the wastes could become overly acidic or alkaline, depending upon in-house plant operations and periodic increases in the flows of certain contributing waste streams. A capability for neutralization of the mixed waste prior to introduction to the bioreactor should, therefore, be provided.

Nutrient adjustment can be accomplished by adding phosphoric acid as required. Nitrogenous compound levels in Influent B should contribute a substantial amount of the nitrogen required for biological metabolism. It is apparent that some additional nutrients, particularly phosphorus, may have to be added to provide an acceptable carbon/nitrogen/phosphorus ratio.

TREATMENT SYSTEM CONSTRUCTION AND DESIGN

Overall System

In constructing the Washburn Tunnel Facility, circular and rectangular sedimentation and aeration basins were excavated and cast. There are 25 aerators (with a total horsepower of 3,390) in the aeration basins; sludge collection equipment is installed in the various clarifiers. Additional equipment includes waste and sludge transfer piping, neutralization facilities, a cooling tower, and sludge handling facilities. The facility also has advanced monitoring equipment and a centralized control station. During 1976, the GCWDA installed a large fluidized bed incinerator.

Figure 30 shows the process flows through the plant. Influents A, B, C, D, and F enter the treatment system through bar screens where large debris is removed. A total flow of approximately 1.7 x 10^5 m^3/day (45 MGD) containing about 55,000 kg (121,254 lb) of BOD is treated each day. The wastes then pass through a grit removal chamber where sand, grit, and other abrasive material settle.

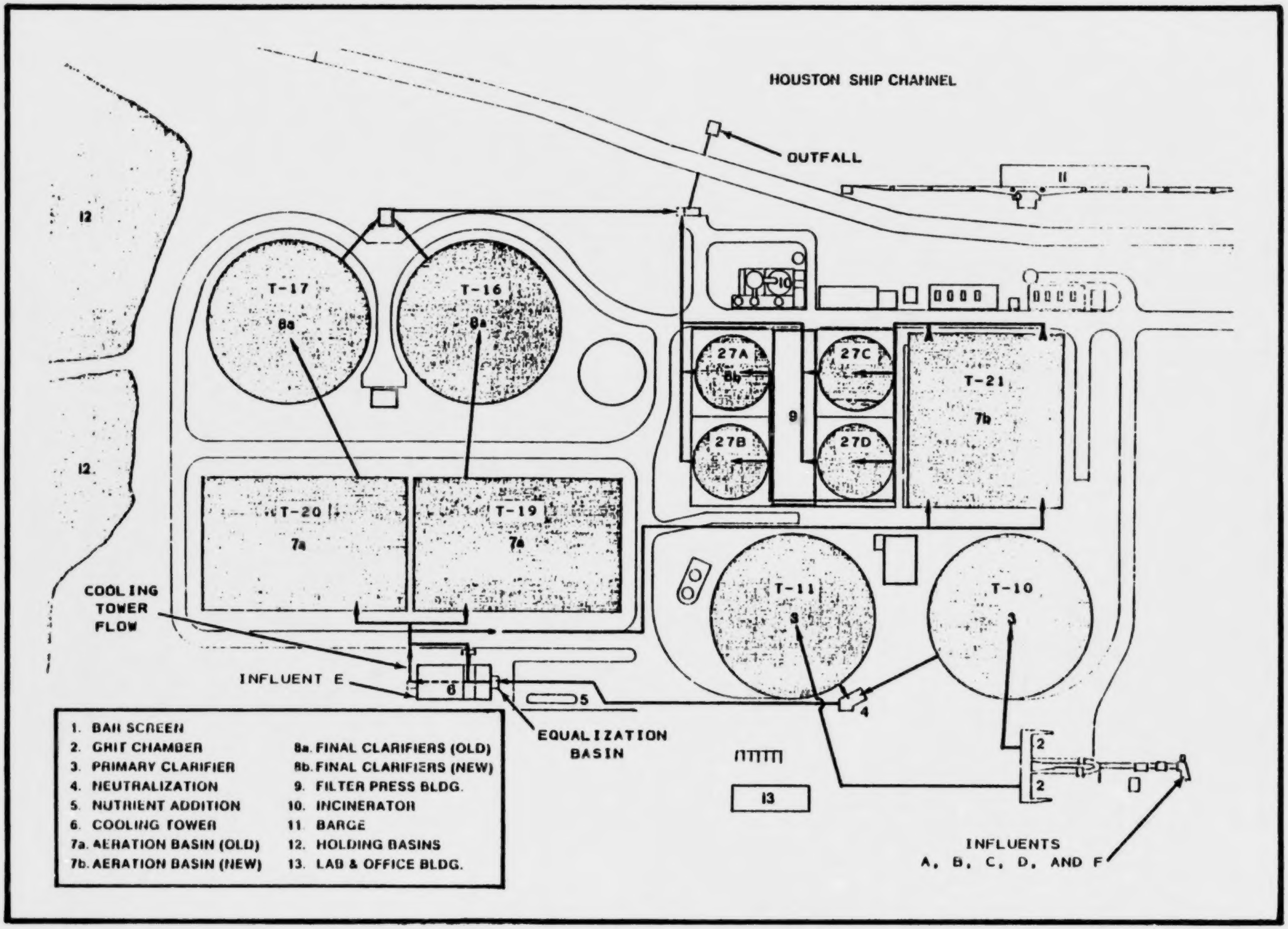

HOUSTON SHIP CHANNEL
OUTFALL
11
12
12
T-17
8a
T-16
8a
10
27A
8b
27B
9
27C
27D
T-21
7b
T-20
7a
T-19
7a
T-11
3
T-10
3
COOLING TOWER FLOW
INFLUENT E
6
5
4
2
2
EQUALIZATION BASIN
13
INFLUENTS A, B, C, D, AND F
1. BAR SCREEN
2. GRIT CHAMBER
3. PRIMARY CLARIFIER
4. NEUTRALIZATION
5. NUTRIENT ADDITION
6. COOLING TOWER
7a. AERATION BASIN (OLD)
7b. AERATION BASIN (NEW)
8a. FINAL CLARIFIERS (OLD)
8b. FINAL CLARIFIERS (NEW)
9. FILTER PRESS BLDG.
10. INCINERATOR
11. BARGE
12. HOLDING BASINS
13. LAB & OFFICE BLDG.

Figure 30. Process flows through the GCWDA Washburn Tunnel facility.

Two 64-meter diameter primary clarifiers (T-10 and T-11) are used to remove suspended solids that settle during the 3-hr retention. A total of 2,722 t (3,000 tons) of primary and biological sludge (1 to 2 percent solids) is removed from the clarifiers each day and wasted to the sludge processing/disposal facilities. The clarified waste then flows to a neutralization basin where sulfuric acid may be added to lower waste alkalinity. Phosphoric acid is added as a nutrient source when necessary; the nitrogen nutrient requirement is provided by ammonia.

A cooling tower is used to cool the waste to about 40°C in the summer. Figure 31 shows views of the cooling tower. A portion of the warm influent may be pumped to the top of the tower and cascaded down onto the redwood impingers. When cooling is not needed, wastewater flows directly to the aeration basins where the waste is completely mixed by surface aerators with sludge recycled from the secondary clarifiers. Figure 30 shows how the waste flow from the equalization basin/cooling tower area is split into two separate flows and channeled to aeration basins T-19, T-20, or T-21. From this point on, there are two parallel but dissimilar secondary biological systems. Lime is occasionally added to the aeration basins for pH adjustment.

From the aeration basins, the biologically treated wastewater flows to the secondary clarifiers. Two 61-m-diameter clarifiers (T-16 and T-17) receive waste flows from aeration basins T-19 and T-21; the four smaller clarifiers (27A through D) receive wastes from aeration basin T-21. Part of the settled solids from the secondary clarifiers is pumped back to the aeration basins, and part is pumped along with sludge from the primary clarifiers to removal, dewatering, and disposal facilities. The biologically treated and clarified effluent then overflows the clarifier weirs and discharges to the Houston Ship Channel.

System specifications for the Washburn Tunnel Facility are shown in Table 71. Approximately 1.33 x $10^5 m^3$/day (3.5 MGD), or 78 percent of the total flow, passes through the primary clarifiers before entering the equalization basin; it is then mixed with the remaining 22 percent of the total flow (Influent E). The flow is then split to the two aeration basins; about 1.17 x $10^5 m^3$/day (3.1 MGD) (69 percent) goes to basins T-19 and T-20 and 5.32 x $10^4 m^3$/day (1.4 MGD) (31 percent) goes to basin T-21. However, these are only estimates, as the relative flows to one basin or the other can be altered.

OPERATIONAL INFORMATION

Data describing the Washburn Tunnel Facility system operations and internal waste stream characteristics came from two sources:

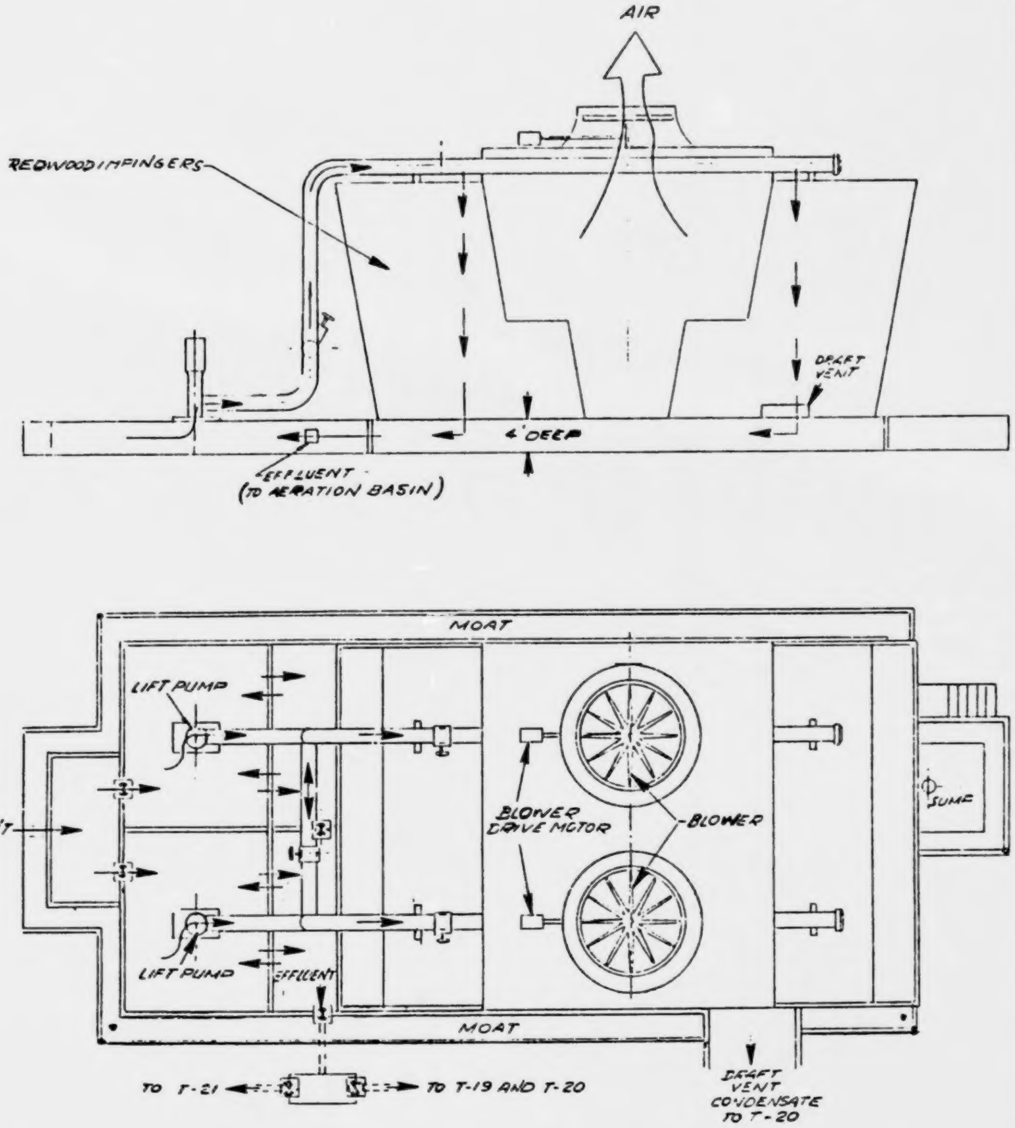

AIR
REDWOOD IMPINGERS
DRAFT VENT
4' DEEP
EFFLUENT (TO AERATION BASIN)
MOAT
LIFT PUMP
INFLUENT
BLOWER DRIVE MOTOR
BLOWER
SUMP
LIFT PUMP
EFFLUENT
MOAT
TO T-21
TO T-19 AND T-20
DRAFT VENT CONDENSATE TO T-20

Figure 31. Washburn Tunnel facility
cooling tower.

TABLE 71. UNIT CAPACITIES: WASHBURN TUNNEL FACILITY

Unit	No. of Units	Width	Diameter	Length	Depth	Volume	Approx. Flow (m^3/d	Retention Time
Primary clarifiers			64 m		4.57 m	15.5 ML		
T-10, T-11	2	--	(210 ft)	--	(15 ft)	(4.1 MG)	132.5×10^3	2.8 hr
Aeration Basins		48.8 m		76.2 m	4.88 m	18.09 ML		
(old) T-19, T-20	2	(160 ft)	--	(250 ft)	(16 ft)	(4.78 MG)	58.7×10^3	7.4 hr
Aeration Basins		56.1 m		64 m	4.57 m	17.0 ML		
(new) T-21	1	(184 ft)	--	(210 ft)	(15 ft)	(4.5 MG)	53.2×10^3	7.7 hr
Final Clarifiers			60.96 m		3.66 m	10.7 ML		
(old) T-16, T-17	2	--	(200 ft)	--	(12 ft)	(2.82 MG)	58.7×10^3	4.4 hr
Final Clarifiers		30-48 m		30.48 m	5.18 m	5.0 ML		
(new) 27A-D	4	(100 ft)	--	(100 ft)	(17 ft)	(1.32 MG)	13.3×10^3	9.1 hr

- Chemical usage records
- Monitoring at specified stations.

Information on the percent of total flow diverted to the various aeration basins, percent sludge wasted, feed rates to the sludge centrifuges, and other important operational specifications were also available.

Monthly chemical usage data are summarized as the average daily consumption for 1976:

Chemical	Average daily consumption (1976)
• Primary polymer	2,837 kg/day (6,255 lb/day)
• Sulfuric acid	1.43 m^3/day
• Phosphoric acid	5.61 m^3/day
• Liquid ammonia	0.70 m^3/day
• Diatomaceous earth	3,906 kg/day (8,621 lb/day)
• Lime	2,555 kg/day (5,634 lb/day)

The sulfuric acid and lime are used for pH control and sludge conditioning. The addition of concentrated phosphoric acid and liquid ammonia at the rates specified above is equivalent to a nitrogen loading rate of 336 kg/day (740 lb/day) as nitrogen and a phosphorus loading rate of 2,948 kg/day (6,500 lb/day) as phosphorus.

Sampling station locations for monitoring internal waste stream characteristics are shown in Figure 32. Temperature, pH, Imhoff settleability, total organic carbon, and suspended solids are measured at the "primary effluent" station, T-31. Sampling is conducted where the clarified aqueous effluents from basins T-10 and T-11 combine. The second internal sampling station for waste stream flow is at the influent to the aeration basins (station AI). Here, only pH and temperature are monitored. Samples taken from stations in aeration basins T-19, T-20, and T-21 are measured for dissolved oxygen, dissolved oxygen uptake (mg of oxygen demand exerted in one hour), mixed liquor and volatile suspended solids, and the sludge volume index.

Average 1976 monthly values for the primary effluent station (T-31) and the aerator influent station (AI) are shown in Table 72. Raw waste influent data for 1976 indicated a pH of 8.0, a TOC of 184 mg/ℓ, and suspended solids of 704 mg/ℓ. The data in Table 72 indicates a neutralization of the pH and 63 and 72 percent reductions in TOC and TSS loading respectively.

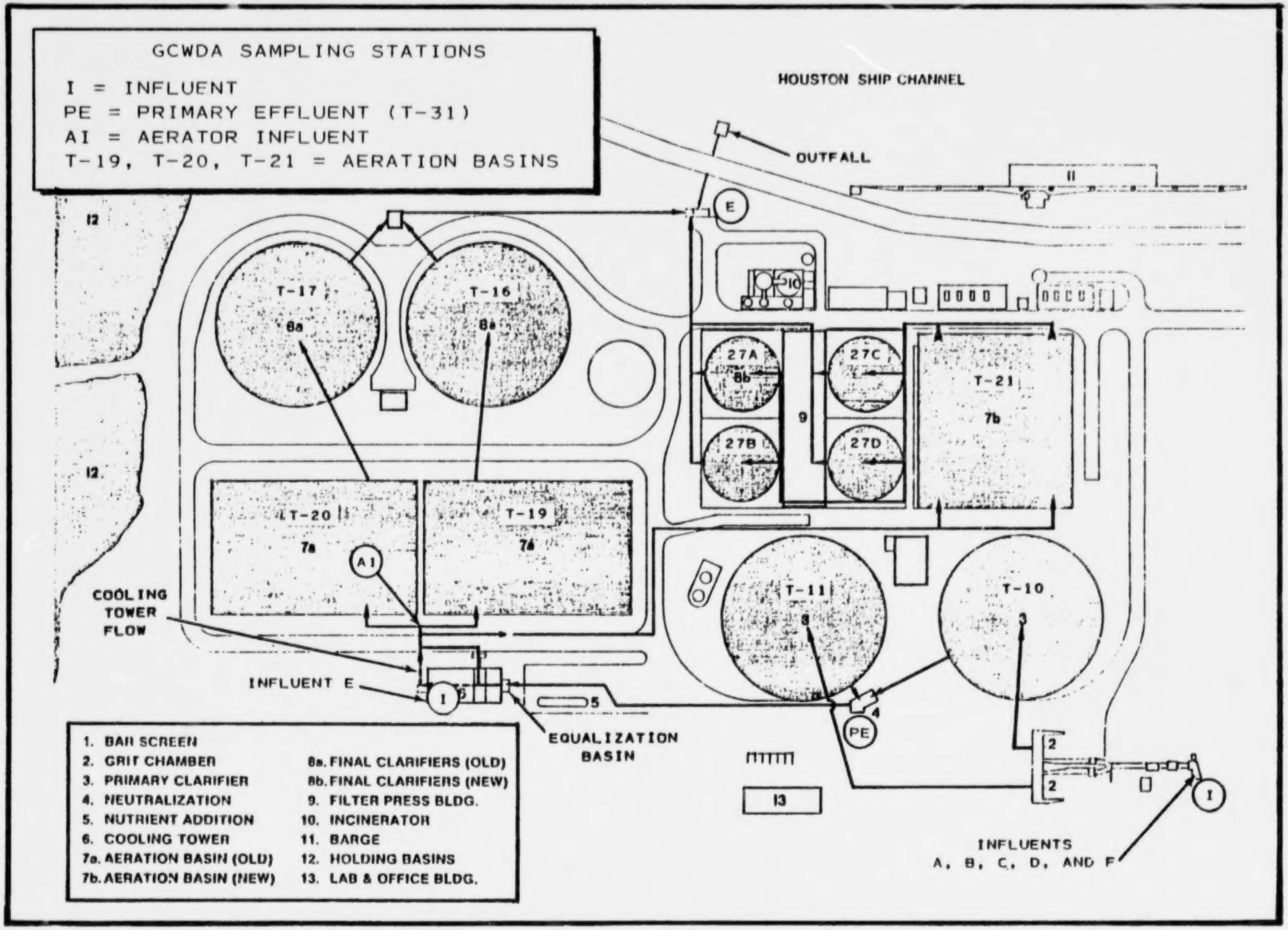

GCWDA SAMPLING STATIONS
I = INFLUENT
PE = PRIMARY EFFLUENT (T-31)
AI = AERATOR INFLUENT
T-19, T-20, T-21 = AERATION BASINS
HOUSTON SHIP CHANNEL
OUTFALL
11
E
12
12
T-17
8a
T-16
8a
27A
8b
27B
27C
27D
9
10
T-21
7b
T-20
7a
AI
T-19
7a
T-11
3
T-10
3
COOLING TOWER FLOW
INFLUENT E
I
6
5
EQUALIZATION BASIN
4
PE
2
2
13
I
INFLUENTS A, B, C, D, AND F
1. BAR SCREEN
2. GRIT CHAMBER
3. PRIMARY CLARIFIER
4. NEUTRALIZATION
5. NUTRIENT ADDITION
6. COOLING TOWER
7a. AERATION BASIN (OLD)
7b. AERATION BASIN (NEW)
8a. FINAL CLARIFIERS (OLD)
8b. FINAL CLARIFIERS (NEW)
9. FILTER PRESS BLDG.
10. INCINERATOR
11. BARGE
12. HOLDING BASINS
13. LAB & OFFICE BLDG.

Figure 32. Washburn Tunnel Facility: GCWDA existing sampling stations.

TABLE 72. 1976 DATA FOR PRIMARY EFFLUENT AND AERATOR INFLUENT

Primary effluent (station T-31)

pH	Temp. ^{o}C	Imhoff ml/ℓ	TOC (mg/ℓ)	TOC kg/day (lb/day)	Suspended solids (mg/ℓ)	Suspended Solids kg/day (lb/day)
7.1	36.8^{o}	1.7	176.6	11,449 (25,245)	194	32,673 (72,044)

Aerator influent (station AI)

pH	Temp. ^{o}C
7.1	36.7^{o}

Data for Station A1 indicate that the pH and temperature of the waste as it enters the aeration basins are similar to those of the waste leaving the primary settling basins. Although the average temperature of the aeration basin influent in 1976 was 36.7°C (98.1°F), the lowest monthly average was in December 31.1°C (88.0°F), while the highest was in August and was 40°C (104°F). The waste temperature appears to be directly related to the ambient air temperature. During the summer, the cooling tower must be used to maintain the influent and aeration basin temperatures at or below 40°C (104°F). Otherwise, undesirable thermophillic microorganisms will be favored in the basins.

Average monthly values at the three aeration basins in 1976 were as follows:

Basin	DO (mg/ℓ)	DO uptake (mg/ℓ)	MLSS (mg/ℓ)	MLVSS (mg/ℓ)	SVI
T-19	3.95	32.75	2,433.33	1,603.25	9.53
T-20	4.03	28.75	2,541.67	1,640.33	8.65
T-21	3.68	32.83	3,291.67	2,107.08	8.89

The total oxygen demand based upon the stated volumes of the various aeration basins was calculated as were the F/M ratio, as kg influent BOD/kg MLSS and as kg influent COD/kg MLSS. Sludge age was determined from (mg/ℓ MLSS) x (basin volume) x (million liters) x (mg/ℓ influent SS)/(flow to basin (ML/DAY). The results were as follows:

Basin	Total oxygen demand (TOD) from DO uptake	F/M ratio (kg BOD/kg MLSS)	F/M ratio (kg COD/kg MLSS)	Sludge age (days)
T-19	14,217 kg/day (31,341.75 lbs/day)	0.4	1.6	1.1
T-20	12,480 kg/day (27,513.75 lbs/day)	0.4	1.5	1.1
T-21	13,388 kg/day (29.514.17 lbs/day)	0.3	1.1	1.5

The calculated F/M ratios are actually somewhat low because of the removal of an unquantified amount of BOD and COD in primary clarification. Nevertheless, the calculated ratio corresponds to a high rate, completely mixed activated sludge system treating industrial wastes. The F/M ratio is calculated on a daily basis to determine necessary adjustments in the rate of sludge return.

An average feed rate to the centrifuges of 142 m^3/day was maintained during 1976. This flow is approximately 9.1 percent solids. Sludge wasted from the primary clarifiers is 1 to 2 percent solids.

TREATMENT EFFICIENCY

Tables 73 and 74 show the average 1976 concentrations and loadings, respectively, for constituents in the Washburn Tunnel Facility effluent. These data are filed monthly as part of the influent/effluent report in compliance with the NPDES discharge permit requirements. The effluent quality should be compared with the influent quality (Tables 66 and 69) to determine overall treatment efficiency. Table 75 shows the results of this comparison in terms of kilograms of constituent removed per day and percent of efficiency.

The graphs in Figures 33 and 34 show the fluctuations of the concentrations and loadings of organic constituents, expressed as TOC, BOD_5, and COD during 1976. Comparison with similar graphs for plant influents (Figures 28 and 29) indicates that all three waste parameters are significantly reduced. The range of reported monthly averages and the lowest and highest reported monthly maximum for any one effluent sample are given below.

Parameter	Range of the monthly averages (mg/ℓ)	Lowest reported monthly minimum (mg/ℓ)	Highest reported monthly maximum (mg/ℓ)
BOD_5	13 - 35	6	76
COD	254 - 388	200	760
TOC	103 - 144	54	313

The average reductions in BOD_5, COD, and TOC for 1976 were 93, 72, and 36 percent, respectively. These efficiencies indicate that a large portion of inert organic material is passing through the system. It is unlikely that this material is phenols or oil and grease, since these constituents are reduced 98 and 88 percent, respectively. Furthermore, the organic materials in the effluent are not readily biodegradable. For example, most (93 percent) of the raw influent BOD_5 is satisfied by the treatment process. There are not sufficient data to provide detailed descriptions of specific discharge organic compounds; further investigations are needed to determine their identity and concentrations.

Comparisons of month-to-month fluctuations in both influent and effluent organic constituents show that the long retention time and complete-mix bioreactor tend to reduce influent fluctuations and provide an effluent of predictable quality. Detailed raw waste characterization, nutrient addition,

TABLE 73. WASHBURN TUNNEL FACILITY - 1976 EFFLUENT QUALITY SUMMARY

Parameter	(mg/ℓ)
BOD	22.9
COD	331.8
TSS	50.7
Oil and grease	3.6
Phenol	0.06
Sulfide	0.11
Cyanide	-
Mercury	-
TOC	117.2
Total Cr	0.06
Color	594.0
NH_3-N	4.4
Fluoride	1.4
Zinc	0.2
Titanium	2.4
NO_3-N	0.8
TKN	9.3
TDS	1856.3
Total P	0.64
Aluminum	2.0
Arsenic	-
Barium	0.17
Boron	-
Cobalt	0.02
Copper	0.04
Iron	1.07
Lead	0.03
Manganese	0.51
Molybdenum	-
Nickel	0.05
Selenium	-
Silver	-
Cadmium	-

TABLE 74. WASHBURN TUNNEL FACILITY - 1976
EFFLUENT QUALITY SUMMARY

Parameter	Average kg/day (lb/day)
BOD	3,868 (85,289)
COD	55,922 (12,308)
TSS	8,582 (18,923)
Oil and grease	620 (1,367
Phenol	10.1 (22.3)
Sulfide	15.6 (34.4)
Cyanide	-
Mercury	-
TOD	19,909.7 (43,901)
Total chromium	10.0 (22.1)
Color	100,757.0 (222,169)
NH_3-N	736 (1,623)
Fluoride	235 (518)
Zinc	38.7 (85.3)
Titanium	409.9 (904)
NO_3-N	134 (295.5)
TKN	1,546.9 (3,411)
TDS	312,463.4 (688,982)
Total P	108 (238)
Aluminum	336.4 (741.8)
Arsenic	-
Barium	28.5 (62.8)
Boron	-
Cobalt	2.9 (6.4)
Copper	8.8 (19.4)
Iron	184.0 (405.7)
Lead	5.2 (11.5)
Manganese	88.0 (194)
Molybdenum	-
Nickel	8.8 (19.4)
Selenium	-
Silver	-
Cadmium	-

TABLE 75. WASHBURN TUNNEL FACILITY: 1976 OVERALL TREATMENT PLANT EFFICIENCY

Parameter	Average kg/day (lb/day removed	Percent efficiency (influent-effluent/influent)
BOD	53,298 (117,522)	93
COD	146,404 (322,821)	72
TSS	110,481 (243,611)	93
Oil and grease	4,695 (10,352)	88
Phenol	652.1 (1,437.9)	98
Sulfide	187.6 (413.7)	92
Cyanide	> 22.9 (>50.5	94
Mercury	> 0.04 (0.09)	20
TOC	11,343 (25,011)	36
Chromium	17.3 (38.1)	63
Color	-19,052	(increase)
NH_3-N	593 (1,307.6)	45
Fluoride	18 (40)	7
Zinc	39.6 (87.3)	51
Titanium	2,036.1 (4,489.6)	83
NO_3-N	503 (1,108)	79
TKN	1,236.5 (2,726.5)	44
TDS	3,035.1 (6,692.3)	1
Total P	99 (218)	48
Aluminum	2,203.0 (4,857.6)	87
Arsenic	-	-
Barium	19.6 (43.2)	41
Boron	-	-
Cobalt	1.3 (2.9)	32
Copper	848.8 (1,872)	99
Iron	673.6 (1,485)	79
Lead	6.4 (14.1)	55
Manganese	44.5 (98.1)	34
Molybdenum	-	-
Nickel	7.1 (15.7)	45
Selenium	-	-
Silver	-	-
Cadmium	-	-

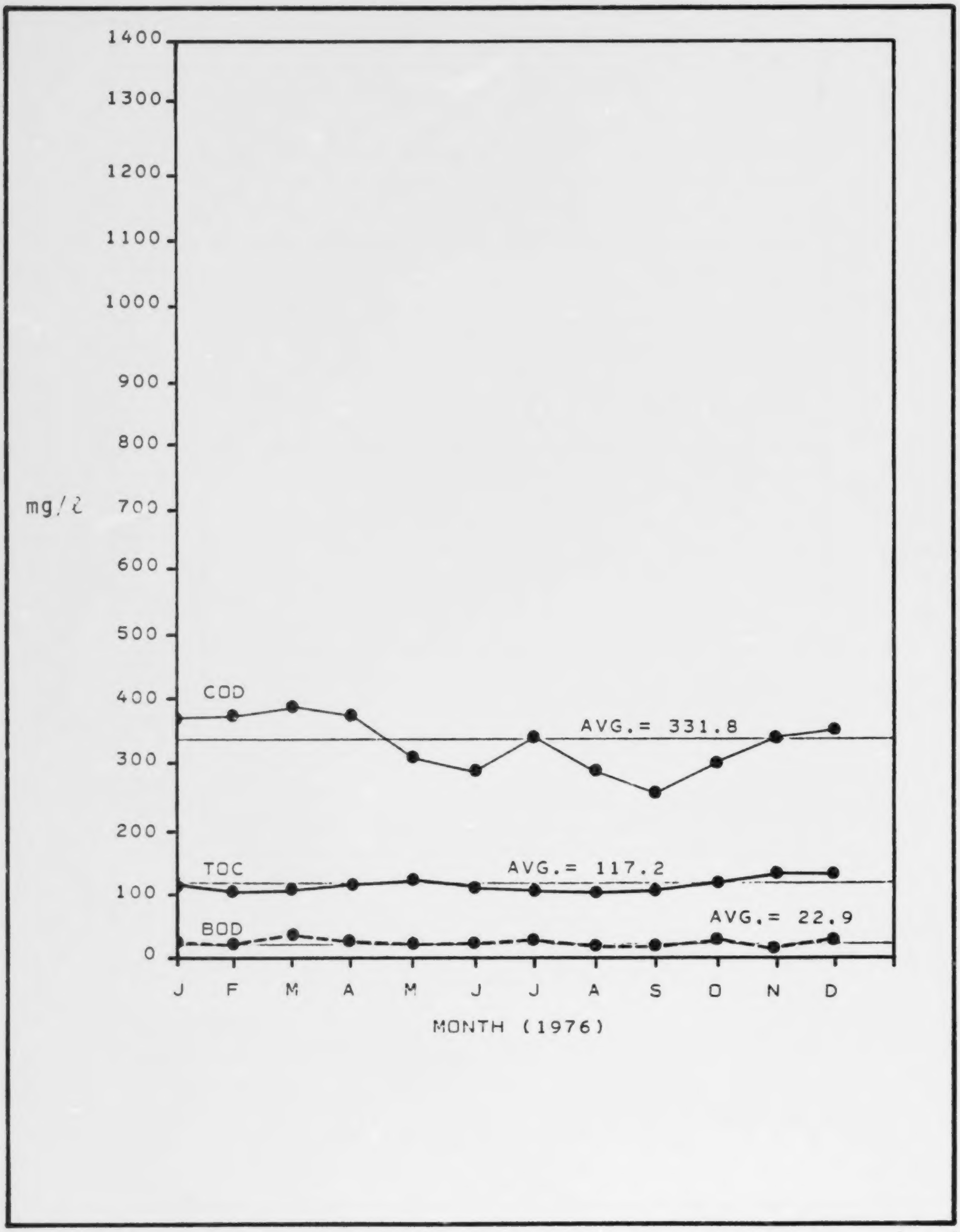


Figure 33. Washburn Tunnel Facility effluent concentrations (ppm) monthly influent/effluent reports - 1976.

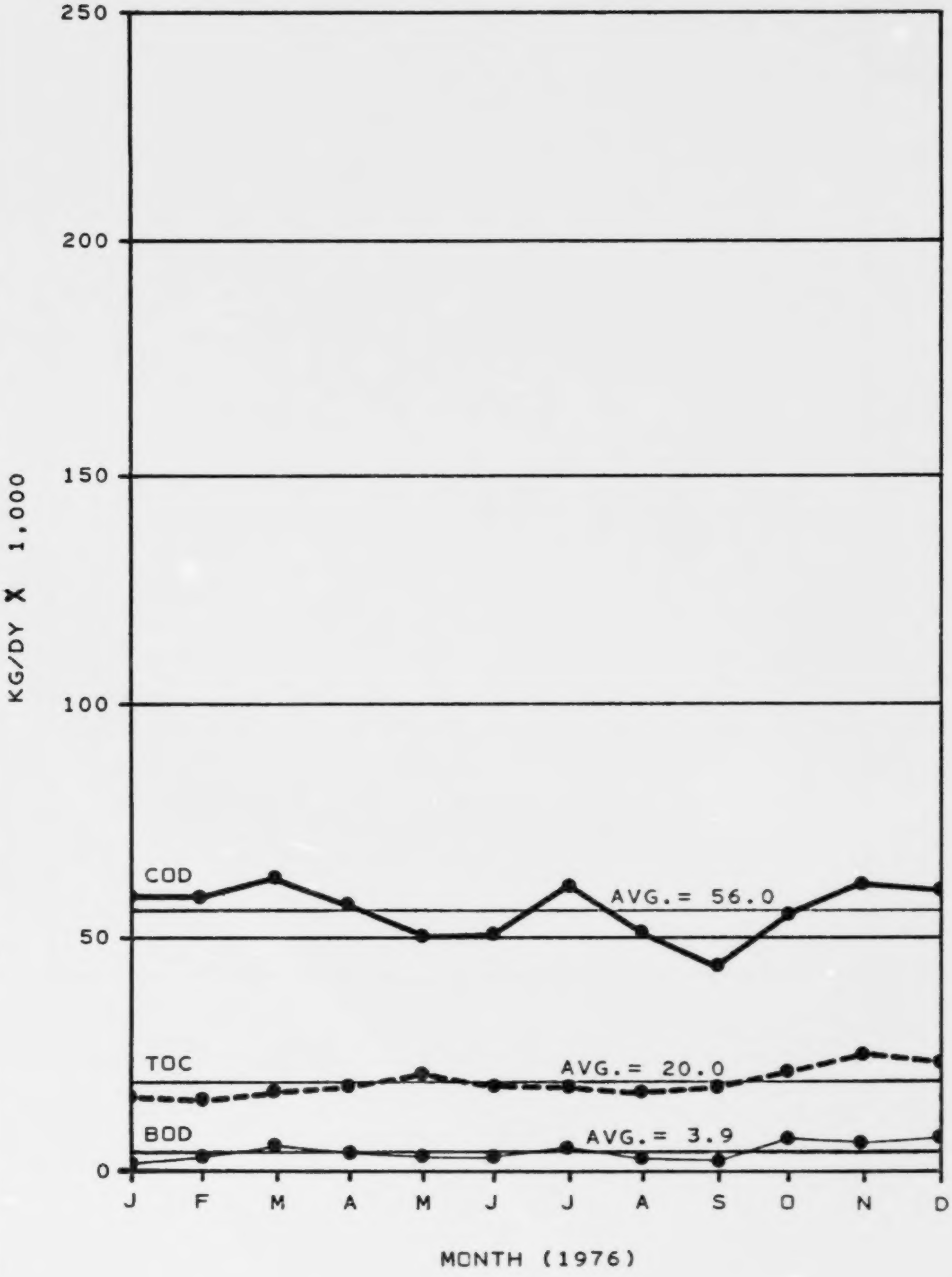


Figure 34. Effluent from Washburn Tunnel treatment plant (avg. 1976 flow = 169.9 x $10^3 m^3$/day).

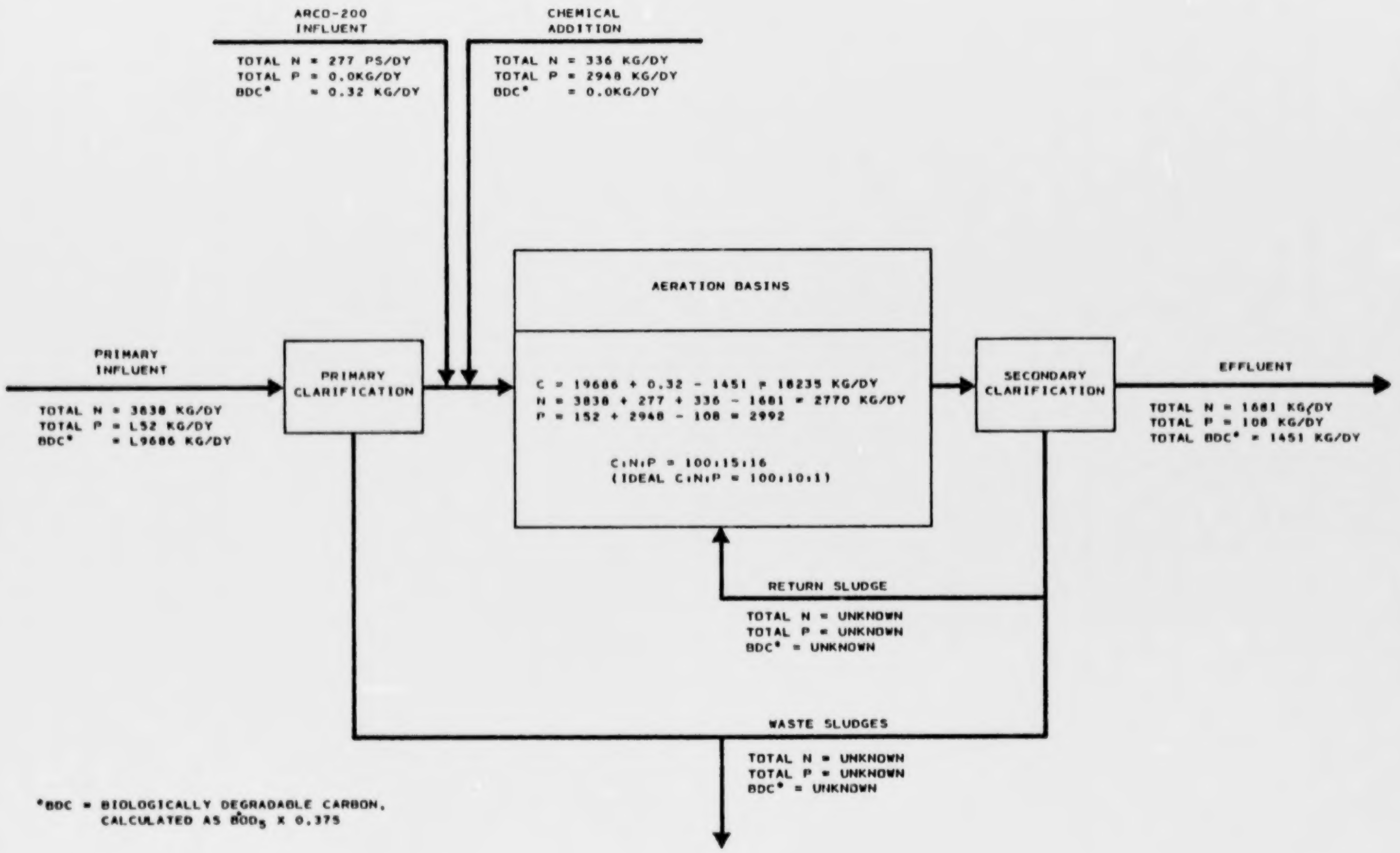
controlled sludge wasting, and high-volume, complete-mix bioreactors with influent temperature control all account for the high BOD removal by the Washburn Tunnel plant.

By evaluating the data describing nitrogen and phosphorus species in the plant influents, chemical additions, and plant effluents, a mass balance for nutrients may be estimated and compared with the amount of carbonaceous material being biologically oxidized in the aerobic treatment process. While such an analysis does not consider the fact that certain types of microbes in the treatment plant may not be able to utilize certain forms of nutrients, e.g., ammonia nitrogen, and nitrogen and phosphorus bound in complex organic molecules, it does indicate the nutrient dynamics of a biological system successfully treating BOD in a complex industrial work.

The majority of the complex organic nitrogen, nitrate nitrogen, and total phosphorus in the process influent originates from the kraft paper mill. Nitrogen, as ammonia, originates from all of the waste contributors. Figure 35 shows the average 1976 loadings for each of the nutrient species from industries and chemical additions at the plant, as well as the loading of biologically degradable carbon. The latter was calculated from BOD loading values by assuming that one mole of oxygen combines with one mole of carbon in aerobic respiration to yield carbon dioxide. As indicated in Figure 35, several important variables necessary for completely characterizing the plant's nutrient balance are presently unquantified. Nutrient removal from the system via primary and secondary sludge wasting is not included. Based upon known influent/effluent quantities, the BOD:N:P ratio of the biooxidation in the aeration basins is approximately 100:9.8:1.6. However, significant removal of phosphorus may be occurring by sorption to sludge in the secondary settling process. This would reduce the estimate for phosphorus, bringing the overall ratio more in line with the 100:10:1 estimate for aerobic bioconversion. Presently, nutrients are added so that trace amounts are continuously detected in the aqueous effluent. Reduction in costs for chemical addition may be achieved by monitoring nutrients in the secondary sludge or adding an influent waste stream rich in phosphorus.

ECONOMIC EVALUATION

The primary settling facilities at the GCWDA Washburn Tunnel Facility were originally constructed by Discharger 1 in 1967. In 1971, a cooling tower, the two older aeration basins (T-19 and T-20), secondary settling basins T-16 and T-17, and sludge centrifuges were added. In May 1973, contracts between the GCWDA and the waste-generating industries were signed and the state called for the sale of $25 million in bonds, of which $12.5 million went to purchase the existing plant. Under agreed terms, the industries are paying all bond amortization, plant


ARCO-200 INFLUENT
TOTAL N = 277 PS/DY
TOTAL P = 0.0KG/DY
BDC* = 0.32 KG/DY
CHEMICAL ADDITION
TOTAL N = 336 KG/DY
TOTAL P = 2948 KG/DY
BDC* = 0.0KG/DY
PRIMARY INFLUENT
TOTAL N = 3838 KG/DY
TOTAL P = L52 KG/DY
BDC* = L9686 KG/DY
PRIMARY CLARIFICATION
AERATION BASINS
C = 19686 + 0.32 - 1451 = 18235 KG/DY
N = 3838 + 277 + 336 - 1681 = 2770 KG/DY
P = 152 + 2948 - 108 = 2992
C:N:P = 100:15:16
(IDEAL C:N:P = 100:10:1)
SECONDARY CLARIFICATION
EFFLUENT
TOTAL N = 1681 KG/DY
TOTAL P = 108 KG/DY
TOTAL BDC* = 1451 KG/DY
RETURN SLUDGE
TOTAL N = UNKNOWN
TOTAL P = UNKNOWN
BDC* = UNKNOWN
WASTE SLUDGES
TOTAL N = UNKNOWN
TOTAL P = UNKNOWN
BDC* = UNKNOWN

*BDC = BIOLOGICALLY DEGRADABLE CARBON, CALCULATED AS BOD_5 X 0.375

Figure 35. Washburn Tunnel Facility: approximation of nutrient balance.

maintenance, and operating costs, plus a management fee to the GCWDA of $120,000 annually.

In 1976, an expansion program was begun which provided the additional biological train (aeration basin T-21) and four secondary settling basins (T-27A, B, C, and D), and sludge handling facilities (filter presses), expanding the plant capacity to approximately 208 million ℓ/d. The total cost of this expansion was $14 million and was financed by the remainder of the original bond issue. The total construction for the entire facility is estimated to be $26 million. A construction cost summary is shown in Table 76. Costs were derived from survey estimates and updating and scaling of estimates for an activated sludge system treating industrial wastewater in the Gulf Coast region as developed by Hovious (66). Specific engineering cost indices were used for updating to 1976 dollars. Estimates for the Washburn Tunnel Plant, where taken from the Hovious data for a 3.8×10^4 m^3/day (1.0 MGD) system, were obtained by multiplying the cited cost data by 4.5. The estimated 1976 operation and maintenance costs for the facility are shown in Table 77. The total cost was $4,332,700. Maintenance costs which were estimated as two percent of total construction cost represent 23 percent of the total operation and maintenance cost. This portion is in agreement with present estimates of between 20 and 25 percent by GCWDA plant officials. Operation labor and supervision was based upon a plant staff of 5 supervisors and 34 laborers. Data on daily chemical usage were used in conjunction with supplier estimates for bulk chemical costs to derive an estimate for the 1976 chemical costs at the facility. Power costs were based upon a ratio of known costs at the GCWDA 40-Acre Facility in Texas City to that facility's total aerator horsepower. Additional miscellaneous power for pumping and sludge raking and processing is not included. The sludge disposal costs are estimated using a unit processing cost per kilogram of BOD removed derived from cost discussions by Hovious (66). The estimate is updated to 1976 dollars.

TABLE 76. WASHBURN TUNNEL FACILITY:
ESTIMATED CONSTRUCTION COST SUMMARY*

Neutralization	
Structural	$ 270,500
Mixing	114,300
Reagent storage	373,700
pH control	147,500
Primary clarification	
Structural	1,519,400
Mechanical equipment	725,300
Equalization	
Structural	960,100
Concrete liner	213,900
Mixing	245,900
Aerobic basin	
Earthwork and roadway	311,000
Concrete liner	1,106,400
Aeration equipment	6,195,700
Aeration equipment support	3,442,080
Electrical support	823,600
Final clarification	
Structural	2,641,800
Mechanical equipment	1,376,800
Piping	1,397,300
Instrumentation	614,700
Building and lab equipment	688,400
Site preparation	347,900
Land at $5,000/acre x 24 acres	120,100
Sub-total	23,636,400
Construction contingency	2,363,600
Construction cost	$ 26,000,000

*Determined from cost estimates for a 37.9 x 10^6 l./d activated sludge plant treating industrial wastes in the Gulf Coast area. 1971 costs were upgraded to 1976 costs using *Engineering News Record* indexes. Costs were then adjusted according to plant size and known total construction cost.

TABLE 77. WASHBURN TUNNEL FACILITY: ESTIMATED O&M COSTS - 1976

Operating labor and supervision • 5 Supervisors • 34 Laborers	$ 480,000
Chemicals	310,000
Power (Aeration HP x 77.78)*	260,000
Maintenance (2 percent of construction)	520,000
Misc. supplies**	6,700
Sludge disposal** ($\mathrm{BOD}_r \times \$0.034/\mathrm{kg}\ \mathrm{BOD}_r \times$ 10 percent annual inflation since 1971)	486,000
Amortize investment*** (20 Years at 6 percent)	2,270,000
Total	$ 4,332,700

cost/kg BOD removed = \$0.223/kg

cost/kg COD removed = \$0.081/kg

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[*] From aeration and power cost data at 40-Acre Facility.

[**] From 1971 data presented in reference 57.

[***] Capital recovery factor = 0.08718. Salvage value not included.

ICI DEEP SHAFT AERATION PROCESS
PARIS, ONTARIO, CANADA

INTRODUCTION

Eco Research Ltd., a wholly-owned subsidiary of Canadian Industries Limited (CIL), has installed an experimental ICI Deep Shaft pilot treatment facility in Paris, Ontario, Canada. This relatively small innovative facility is operated by Eco Research Ltd. and treats a portion of the industrial/domestic blend of wastewater received at an extended aeration sewage treatment plant. The Eco facility is located adjacent to the final clarifier of an extended aeration plant operated by the Ministry of Environment of the Province of Ontario. Industrial/municipal influent into the STP is separated by a splitter box and a portion sent to the Deep Shaft plant. This facility is capable of treating 4.7×10^2 m^3/day (0.2 MGD) of difficult-to-treat industrial/domestic blends, with a total retention time of 30 min. The industrial waste components are received from 14 sources; the major contribution is a textile plant.

The Deep Shaft Process is a secondary biological process utilizing a totally enclosed subsurface aeration shaft. Fluid pressure increased with depth creates increased oxygen solubility and enhances the oxygen transfer efficiency.

HISTORY

The original research and development work for the ICI Deep Shaft Process was carried out in Britain by Imperial Chemical Industries Ltd. (ICI), the parent company of CIL. In early 1974, ICI constructed a prototype Deep Shaft Plant at the site of an existing municipal sewage treatment plant at Billingham in the northeast of England. This plant treated a small portion of the flow to the main sewage treatment plant. The effluent from the prototype was returned to the main plant. Experimentation continued until April 1975, when the Deep Shaft Process was made commercially available. The first plant was sold to an industrial client, Emsland Starke of Emlichheim, West Germany.

The plant at Emlichheim has been operational since October 1975. It is an industrial pretreatment facility that reduces the strength of potato waste prior to discharge to a lagoon system.

Another Deep Shaft demonstration facility is in operation at Molson's Brewery in Barrie, Ontario, Canada. This plant is designed to treat approximately 3.4 x 10^2 m^3/day (0.9 MGD) of brewery waste and has been operating successfully since mid-February 1977.

The treatment facility at Paris, Ontario, was designed and constructed in 1976 by Eco Research Ltd. as a research and development facility. The facility treats a portion of the industrial/domestic blend of wastewater received at the Paris sewage treatment plant operated by the Ontario Ministry of the Environment. Eco Research Ltd. has developed an alternative approach to the separation of solids from that used by its parent company in Europe. The process as developed by ICI utilizes conventional gravity clarification following the Deep Shaft Process. However, because of extremely high dissolved gas content in the effluent passing from the shaft, degassing equipment is required between the clarifier and the shaft. The alternative approach developed by Eco Research Ltd. which proved to be more cost effective uses a flotation unit to remove the solids from the effluent leaving the Deep Shaft.

The Paris facility has been in existence since July 1976 and has performed considerable R&D work related to solids separation. Because this work was time-consuming and because of the high industrial component in the influent, the Deep Shaft Process did not achieve optimization until March 1977. The demonstration facility then operated on a continuous basis for six months, from March to July 1977. Additional research will be performed at the facility in 1978.

Location

The Eco Research facility is located in a residential area in Ontario (Figure 36). The site is on the east bank of the Grand River, which is the receiving water for the MOE extended aeration discharge. Paris (population 7,500) is located approximately 60 km southwest of Toronto, Ontario. Figure 37 is a local map of the Paris area.

Regional Characteristics

The physical surroundings of the Paris ICI facility consist of relatively flat, rolling farmlands. The annual total precipitation is in excess of 102 cm/yr, and the temperature ranges from subzero during winter months to low and mid thirties (degrees centigrade) during summer months. The completely enclosed facility is minimally affected by abiotic factors of temperature change and rainfall.

WASTEWATER IDENTIFICATION

For a number of reasons wastewater chemical characterization for the Paris facility is presently limited. Since there has not

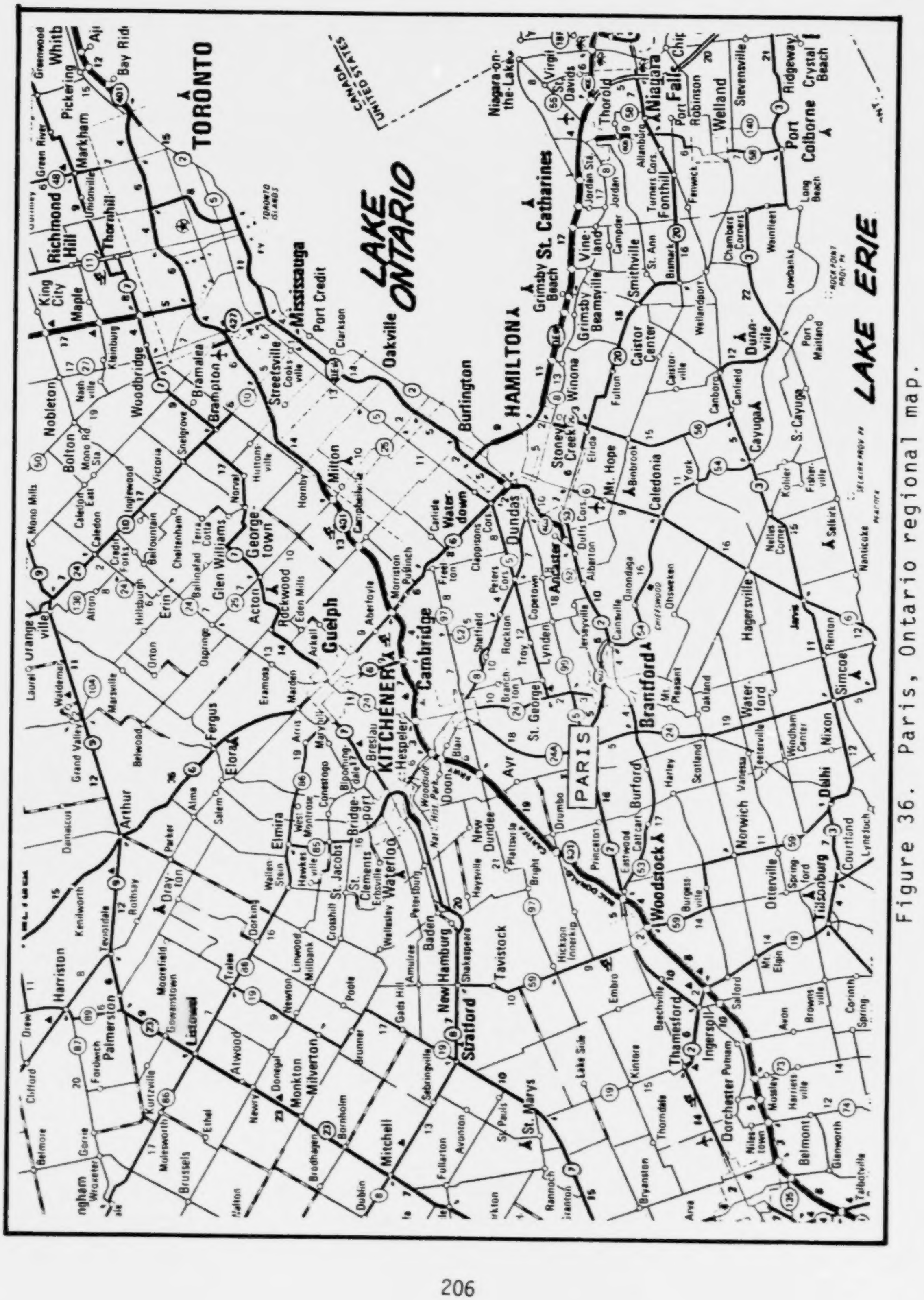

LAKE ONTARIO
LAKE ERIE
TORONTO
HAMILTON
PARIS
Brantford
KITCHENER
Cambridge
Guelph
Waterloo
Stratford
Woodstock
St. Catharines
Niagara Falls
Welland
Port Colborne
Mississauga
Oakville
Burlington
Milton
Brampton
Dundas
Ancaster
Caledonia
Simcoe
Tillsonburg
Ingersoll
Delhi
Dunnville
Cayuga
Hagersville
Waterford
Fergus
Elora
Acton
Georgetown
Orangeville
Arthur
Listowel
Mitchell
St. Marys
Palmerston
Harriston
New Hamburg
Ayr
St. George
Burford
Norwich
Grimsby
Smithville
Niagara-on-the-Lake
CANADA
UNITED STATES

Figure 36. Paris, Ontario regional map.

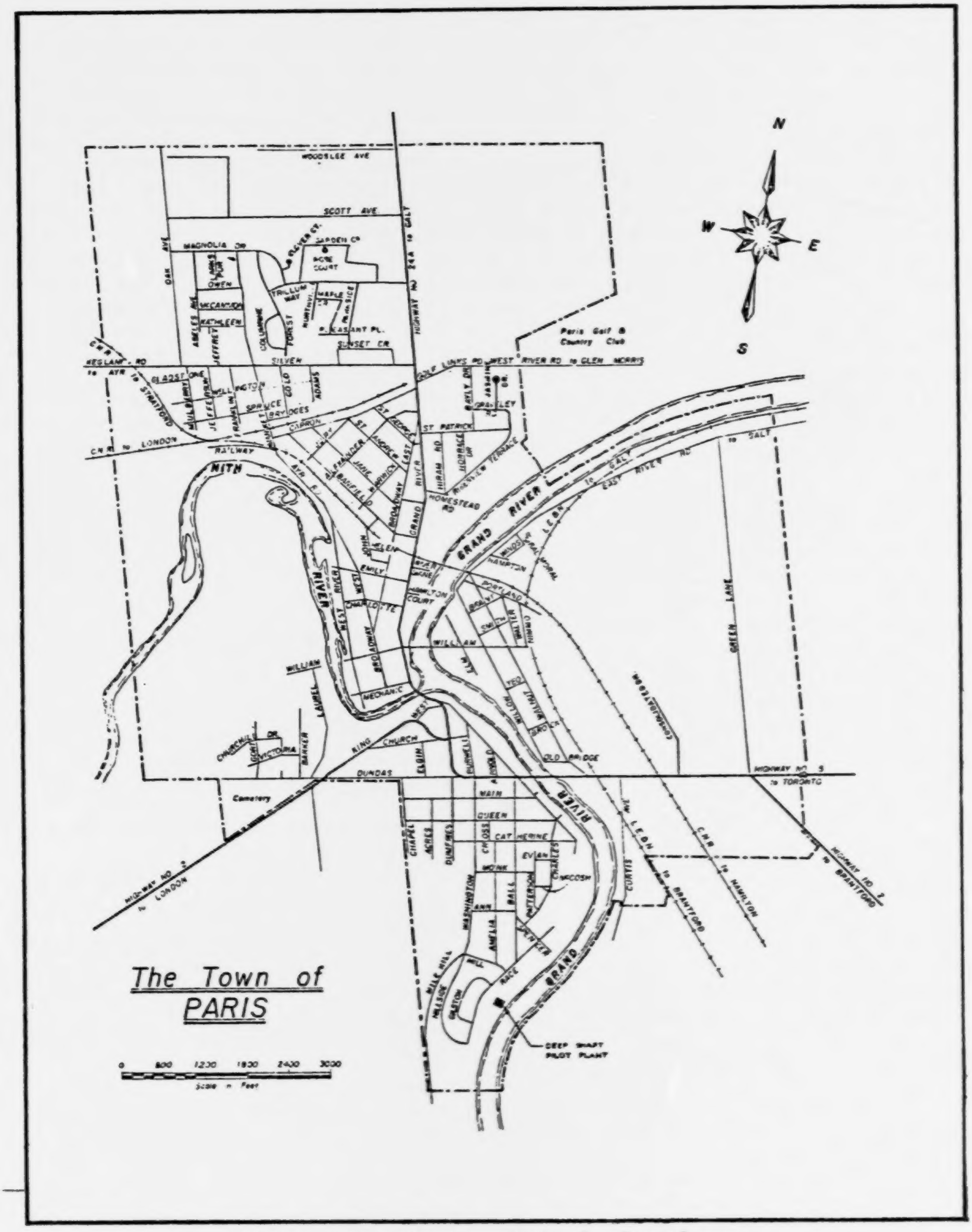

The Town of PARIS
N
S
E
W
0 600 1200 1800 2400 3000
Scale in Feet
WOODSLEE AVE
SCOTT AVE
HIGHWAY NO 24A to GALT
Paris Golf & Country Club
GOLF LINKS RD
WEST RIVER RD to GLEN MORRIS
CNR to AYR & STRATFORD
CNR to LONDON
RAILWAY
NITH RIVER
GRAND RIVER
EAST RIVER RD
LEAN
to GALT
to SALT
GREEN LANE
HIGHWAY NO 5 to TORONTO
HIGHWAY NO 2 to BRANTFORD
HIGHWAY NO 2 to LONDON
CNR to HAMILTON
LEON to BRANTFORD
DUNDAS
Cemetery
MAIN
QUEEN
CATHERINE
WILLIAM
MECHANIC
CHURCH
KING
GRAND RIVER ST
BROADWAY
SILVER
MAGNOLIA DR
OAK AVE
OWEN
KATHLEEN
SUNSET CR
PLEASANT PL.
TRILLIUM WAY
ST PATRICK
HOMESTEAD RD
RIVERVIEW TERRACE
HAMILTON COURT
PORTLAND
OLD BRIDGE
CHARLOTTE
EMILY
WASHINGTON
DEEP SHAFT PILOT PLANT

Figure 37. Paris, Ontario local map.

been regular monitoring for specific organic constituents, exact chemical constituents of influent streams from each contributing industry have not been analyzed. This makes it impossible to compile comprehensive influent summaries. Also, the plant has only been operating in the present mode for several months, so a limited amount of waste data is available. Nevertheless, the limited waste characterization data can be qualitatively augmented by identifying the types of on-line industries and the kinds of process wastes issuing from each industry. The general process waste categories from the 14 industrial contributors are: textile, (approximately 60 percent of the total industrial flow), pharmaceutical, food processing, petrochemical, and printing. The typical wastes associated with the contributing industries are numerous and comprised of many organic and inorganic chemical constituents. An exhaustive literature review resulted in an extensive list of general categories and quantities of organic wastes that might originate from each industrial contributor. Representative compounds, listed below, were chosen on the basis of solubility, polarity, and amenability to gas/liquid chromatography:

- Benzene
- Phenol
- Toluene
- Butanol
- Ethylene dichloride
- Methanol
- Isopropanol
- Carbon tetrachloride

These compounds are a small fraction of the troublesome organic constituents in the waste stream. Thus, the resulting analysis of these compounds does not provide conclusive data on the characterization of this industrial/municipal wastewater.

Table 78 is a record of parameters monitored at the Deep Shaft pilot facility during the months, March to July 1977; Table 79 lists influent monitoring data for the month of May 1977. The influent stream is monitored daily for the following parameters: TSS, BOD_5, soluble BOD_5, and COD. Samples are collected by a composite sampler that siphons incremental aliquots at a predetermined time interval. Figure 38 is a graph of the fluctuating BOD loading rates; such fluctations indicate the need for a composite scanning program in order to estimate average influent BOD loading.

Amenability to Biological Treatment

Characteristics of the Deep Shaft raw influent waste that could adversely affect biological treatment are:

- High pH values and fluctuations
- Presence of refractory compounds
- Presence of surfactants

TABLE 78

DEEP SHAFT FACILITY: PARIS, ONTARIO

WEEKDAY (7 DAY) OPERATION

(March 4 - July 15, 1977)

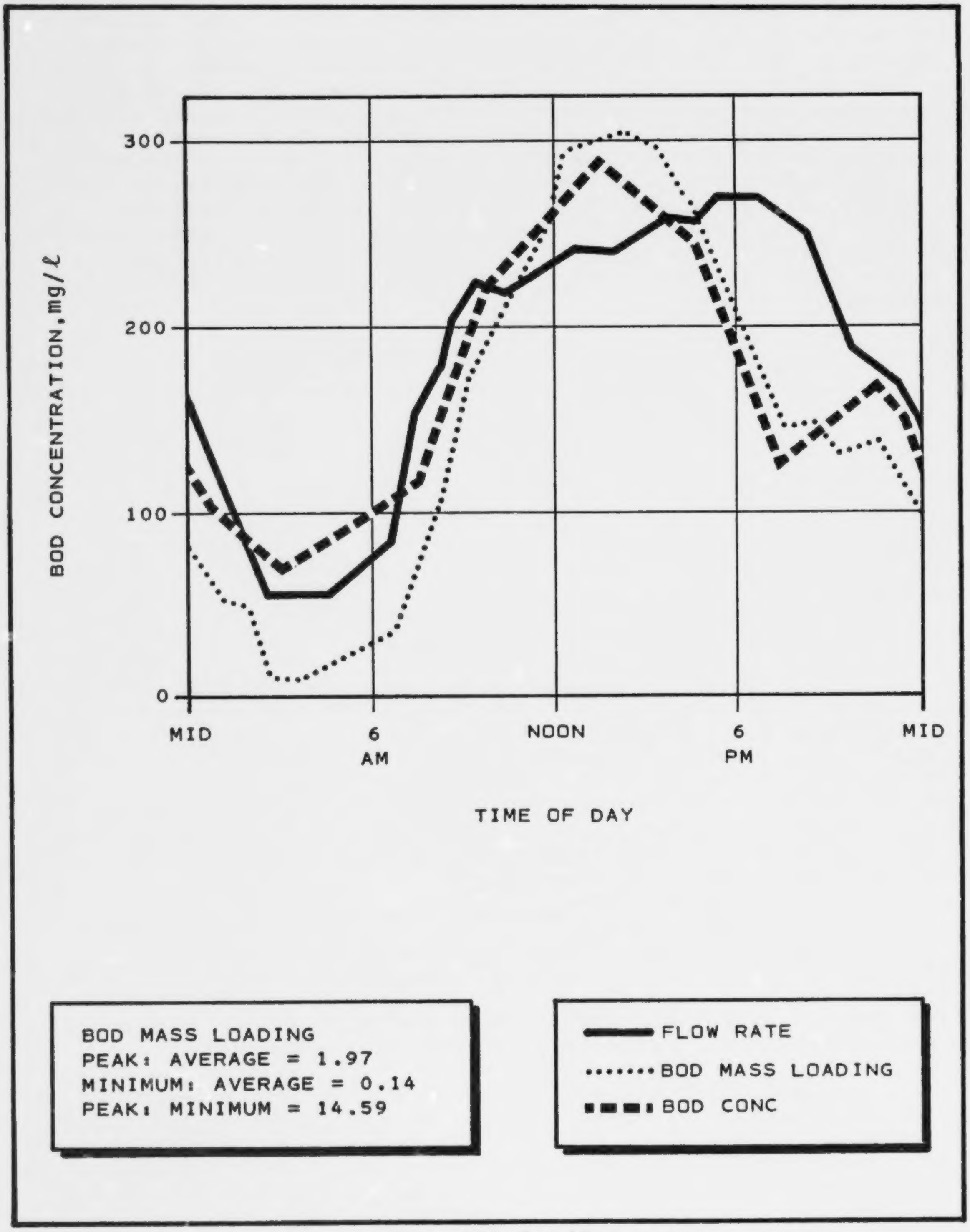
INLET	AVERAGE (ppm)	RANGE (ppm)	DATA POINTS /134 (days)
BOD_5	141	46 - 365	94
$SBOD_5$	53	9 - 138	93
Whole COD	514	216 - 1264	60
TSS	217	75 - 726	92

OUTLET	AVERAGE (ppm)	RANGE (ppm)	DATA POINTS /134 (days)
BOD_5	24	7 - 96	95
$SBOD_5$	15	1 - 56	96
Whole COD	89	25 - 638	67
TSS	29	10 - 121	94

TABLE 79. DEEP SHAFT FACILITY, PARIS, ONTARIO: MAY 1977 INFLUENT MONITORING DATA (mg/ℓ)

Day	SS	BOD_5	Soluble BOD_5	COD
1	124	90	19	238
2	194	195	84	-
3	Laboratory technician ill			
4				
5				
6	209	116	24	-
7	Sampler failure			
8				
9	229	182	86	565
10	182	180	86	531
11	291	224	91	805
12	218	204	86	610
13	226	-	43	479
14	193	141	24	418
15	176	116	20	410
16	314	195	92	652
17	191	169	84	507
18	233	180	93	579
19	208	213	114	698
20	219	102	23	-
21	177	107	23	307
22	139	102	20	224
23	117	113	13	513
24	208	160	76	702
25	270	167	77	582
26	203	202	85	618
27	Sampler failure			
28				
29				
30	456	262	96	1,264
31	209	204	92	604
Total	4,886	3,624	1,451	11,292
Average	212.4	164.7	63	564.6
Corrected Average	208.5	154.5	54	533.1

May 10-12 - Discovered problem with design of flotation tank.
Underflow recycle sump can allow buildup of sludge and prevent proper sludge removal. Problem was overcome at Paris with preventative maintenance.
May 10-12 data deleted from corrected average (DFCA).
May 18-24 - Exceptionally heavy textile loads - (DFCA).
May 31 - Overnight power failure - plant down 8 hours - (DFCA).



BOD MASS LOADING
PEAK: AVERAGE = 1.97
MINIMUM: AVERAGE = 0.14
PEAK: MINIMUM = 14.59

Figure 38. BOD loading rates.

The blending of domestic sewage and other unique wastes in the Paris facility influent results in specific treatment benefits. One of these benefits is nutrient balance, in which nitrogen (NH_3) from the textile mill effluent and phosphorus (orthophosphate) from municipal waste and other sources are added to the predominately carbonaceous chemical plant wastes. Another benefit is dilution of the high strength industrial components in the waste stream. Dilution may reduce the problems of shock loading, enzymatic inhibition, and destruction of cellular membranes associated with elevated toxin or heavy metal concentrations. Monthly averages for the concentrations of parameters in the Paris influent were calculated from the May 1977 daily reports:

Parameter	Avg. concentration in influent (mg/ℓ)
BOD_5	164.7
COD	564.6

The ratio of COD to BOD is 3.4, indicating that a portion of the dichromate oxidizable material is not amenable to rapid degradation by a biological system. Such a condition is typical of industrial waste streams, which usually exhibit a COD/BOD ratio of between 3.0 and 6.0.

TREATMENT SYSTEM CONSTRUCTION AND DESIGN

The Paris facility uses conventional construction in addition to the innovative aeration shaft. This shaft has unique design and operational structures that differentiate the Deep Shaft facility from other secondary biological systems. (Figure 39 is a basic floor plan of the facility.) One unique aspect of the facility is its minimal land requirement, a fraction of that required by other types of treatment facilities. This highly reduced land requirement is an asset, especially where new plant construction is considered for urban areas.

The head tank and air-flotation tank are housed inside a structure of three steel trusses and wood framing with a corrugated metal roof and siding. The structure rests on a 25 cm steel reinforced concrete slab foundation (Figure 40). The housing covers approximately 232 m^2 and shelters all equipment (except the surge tank) necessary for plant operation.

The Deep Shaft was drilled through alternating layers of limestone and shale; bedrock was found 1.8 to 2.7 m (5.9 to 8.9 ft) below the surface. A 20.3 cm (51.0 in) pilot shaft was drilled to a depth of 161.5/m (530.0 ft). Two types of drilling technology were used in "reaming-out" the pilot hole. The initial 30.8 m drilling (81.6 cm in diameter) was accomplished with a cable tool

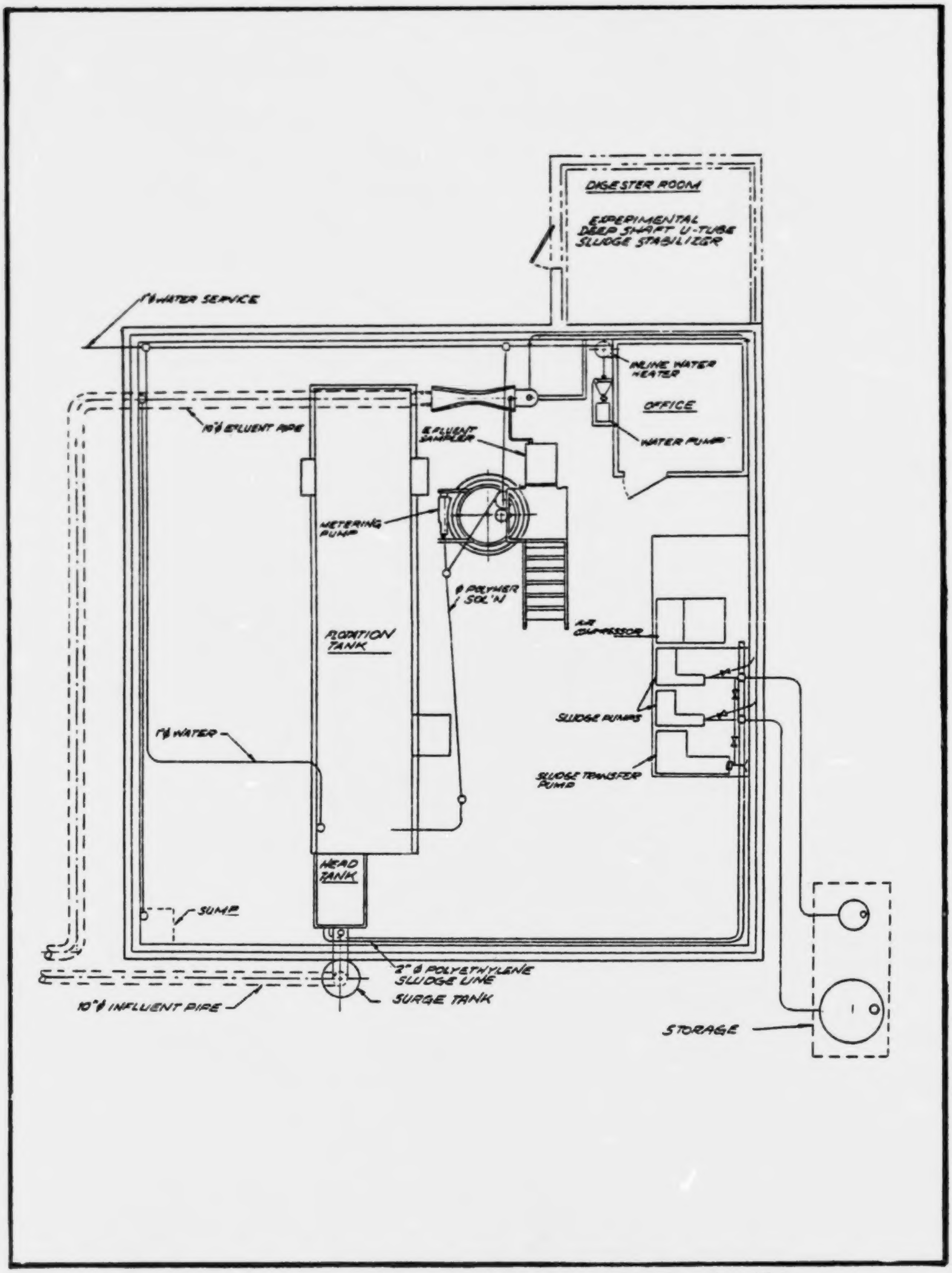

DIGESTER ROOM
EXPERIMENTAL DEEP SHAFT U-TUBE SLUDGE STABILIZER
1"ϕ WATER SERVICE
INLINE WATER HEATER
OFFICE
10"ϕ EFLUENT PIPE
EFLUENT SAMPLER
WATER PUMP
METERING PUMP
ϕ POLYMER SOL'N
AIR COMPRESSOR
FLOTATION TANK
SLUDGE PUMPS
1"ϕ WATER
SLUDGE TRANSFER PUMP
HEAD TANK
SUMP
2" ϕ POLYETHYLENE SLUDGE LINE
SURGE TANK
10"ϕ INFLUENT PIPE
STORAGE

Figure 39. Plan view of the Deep Shaft facility.

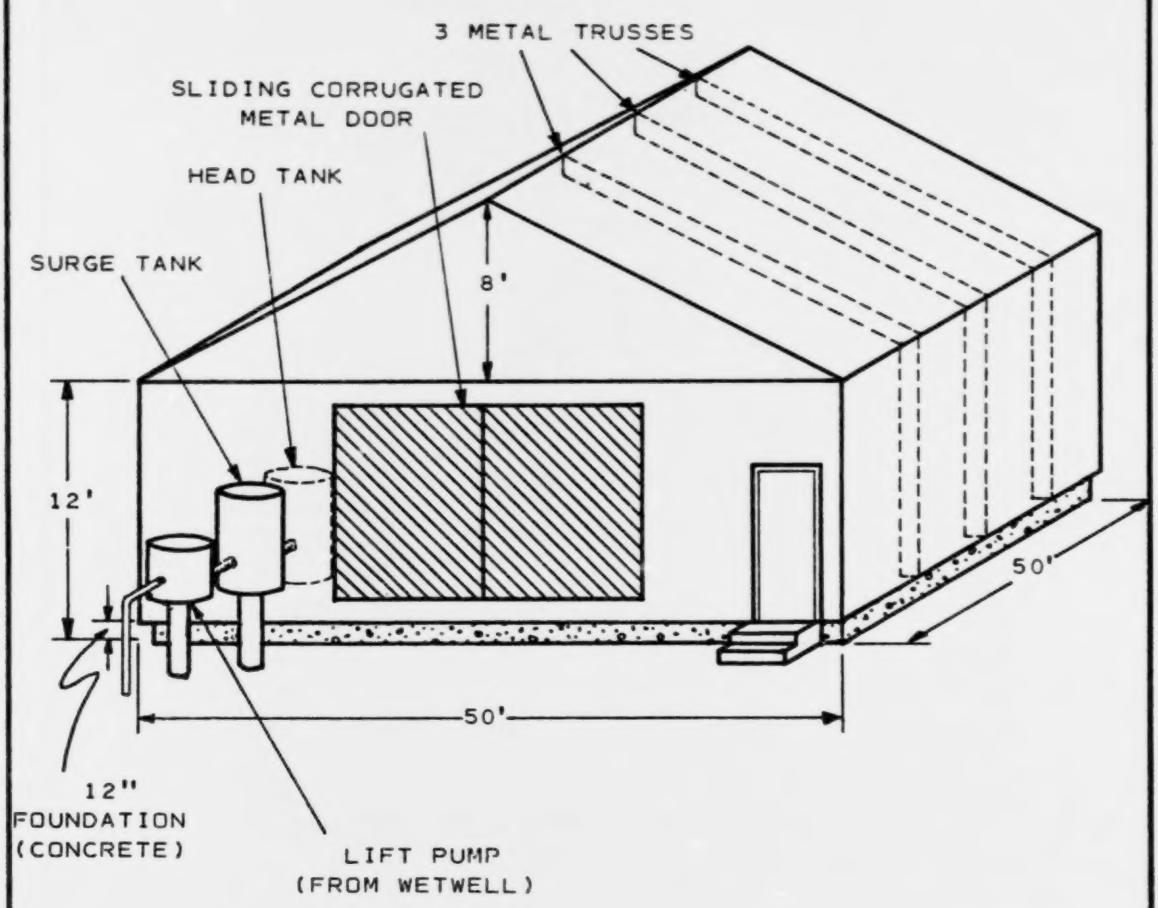

3 METAL TRUSSES
SLIDING CORRUGATED METAL DOOR
HEAD TANK
SURGE TANK
8'
12'
50'
50'
12" FOUNDATION (CONCRETE)
LIFT PUMP (FROM WETWELL)

Figure 40. Sketch of the Deep Shaft structural housing.

passes over a weir as the final effluent, which is presently returned to the headworks of the MOE extended aeration treatment plant.

The Deep Shaft process is a high-rate biological process for the treatment of biodegradable industrial effluents and municipal sewage. The process originated from basic aerobic fermentation technology developed by ICI while researching the production of single cell protein from methanol (19). The use of air for both the biological oxidation requirements and the driving force for liquid circulation is a key to the process. Inherent in the process is the ability to achieve high oxygen mass transfer rates compared to conventional aeration processes. The shafts are designed to make maximum use of improved oxygen mass transfer (19). The same air that is added for BOD removal and circulation also provides the driving force for solids separation in the flotation tank.

The Deep Shaft effluent treatment process is essentially a secondary, plug-flow, complete mix, subsurface aeration basin utilizing a 155-250 m deep shaft. In all effluent treatment processes mass transfer is very important with respect to oxygen and substrate. These concerns are minimized in the Deep Shaft Process, and the tratment rate is generally governed by the biodegradability of the substrate. This is accomplished with better power economy because of high oxygen utilization and transfer efficiencies. In the Deep Shaft process, the dissolved oxygen is approximately ten times that in conventional processes. The highly turbulent flow in the shaft aids in mixing and promotes highly dispersed substrate growth and oxygen in a uniform suspension of small biological floc. This may explain, in part, the high F/M ratio at which Deep Shaft can operate without adversely affecting flocculation (21). In the Deep Shaft system with a depth exceeding 100 m (330 ft), the residence time of the bubbles will be several minutes, and the effect described by Henry's Law (i.e. greater with increasing depth) is so great that most bubbles will go into solution in the lower regions of the shaft depending upon the depth and nature of the waste being treated. Therefore, all the oxygen absorbed will depend upon the biological metabolic rate rather than on the physicochemical transfer rate (63).

At the Paris facility, influent waste is taken from the existing sewage treatment plant after screening and degritting. The waste stream is introduced into the shaft at the top of a vertical tube which extends to the bottom of the shaft; the waste flows down the tube and rises in the annular section between the type and the shaft lining, the downcomer and riser, respectively (Figure 41). The waste makes several cycles around the shaft before a portion passes by gravity into the flotation tank.

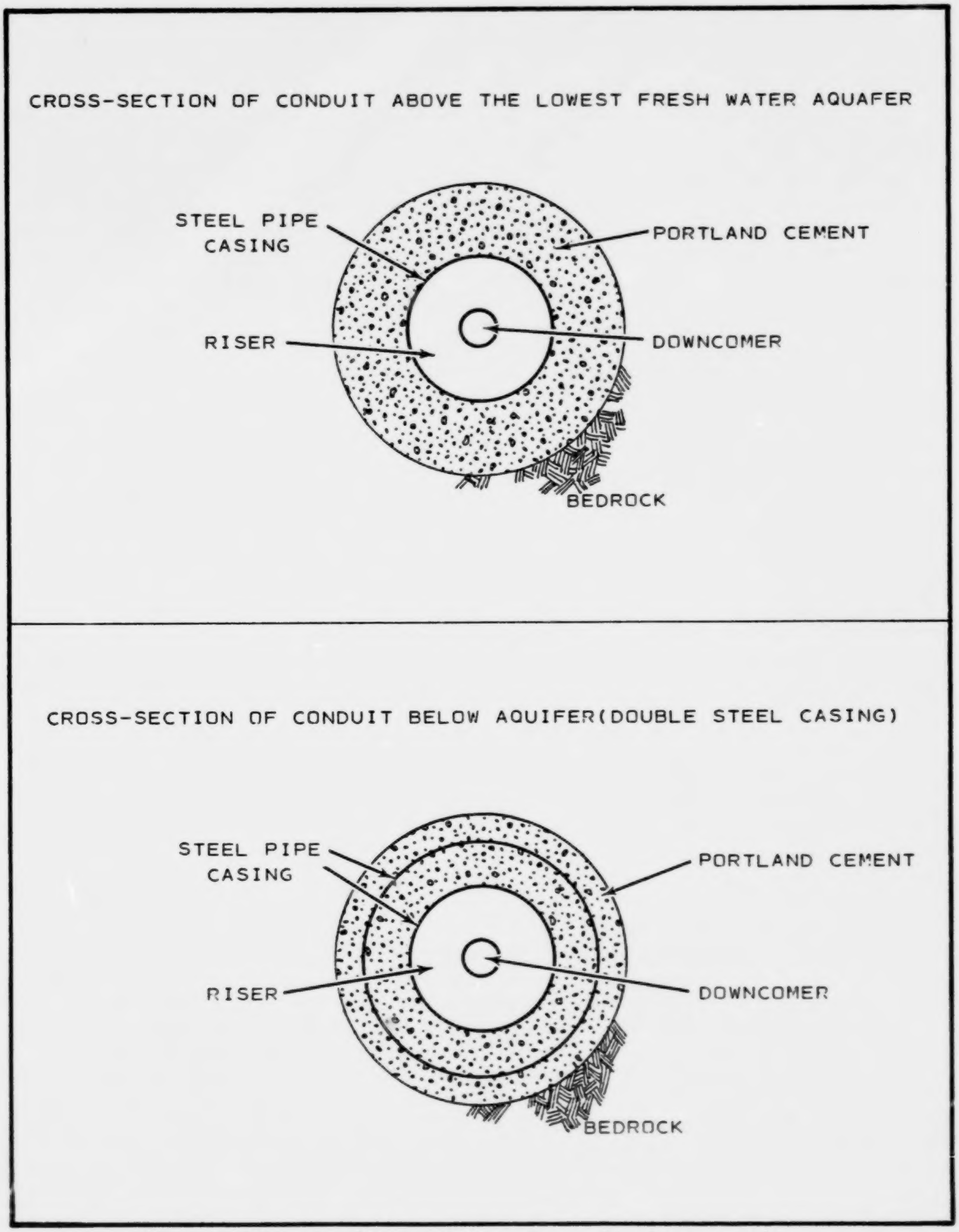

CROSS-SECTION OF CONDUIT ABOVE THE LOWEST FRESH WATER AQUAFER
STEEL PIPE CASING
PORTLAND CEMENT
RISER
DOWNCOMER
BEDROCK
CROSS-SECTION OF CONDUIT BELOW AQUIFER(DOUBLE STEEL CASING)
STEEL PIPE CASING
PORTLAND CEMENT
RISER
DOWNCOMER
BEDROCK

Figure 41. Sealing of the Deep Shaft conduit.

which, because of undersized equipment, later caused problems in reaching the prescribed depth. The remainder of the pilot shaft was bored to a depth of 161.5 m (530.0 ft) at a diameter of 55.9 cm (22.0 in), using rotary drilling procedures (29).

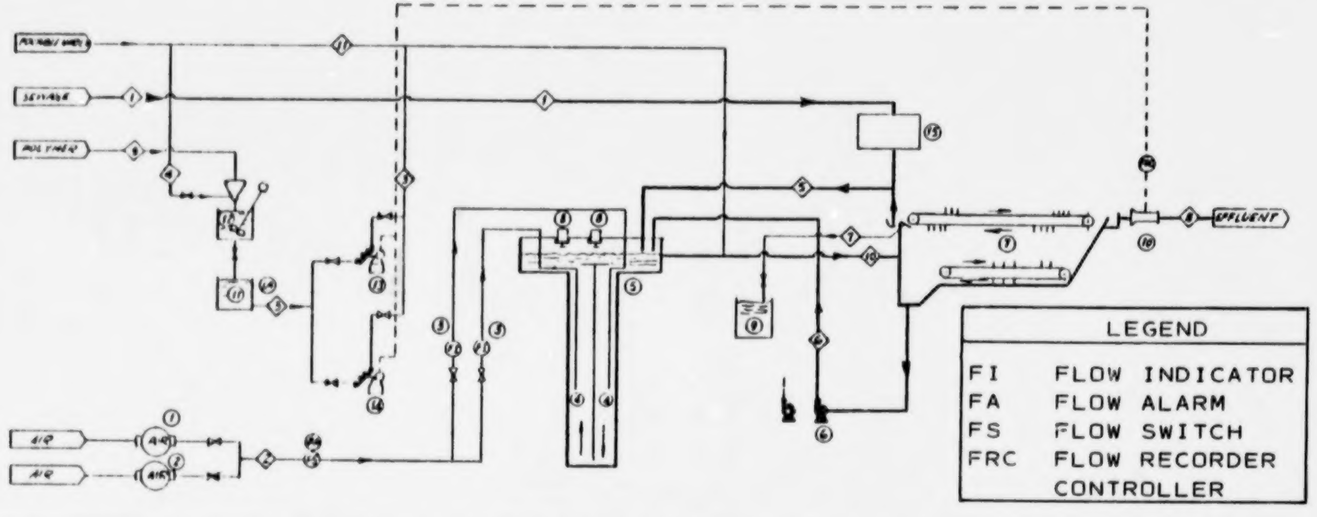
A series of surface casings were used in the upper portion of the shaft to provide support for the rig during construction and provide additional protection to ensure the integrity of the shafts. All cases are grouted to the formation with Portland cement. Figure 41 shows a simplified top view of the shaft casing arrangement.

When considering the structural integrity of the shaft, it is apparent, barring major geologic events, that the construction techniques and proper subsurface testing and siting should provide ample protection against accidental contamination of the surrounding groundwater systems. The shaft has a length of 154.8 m (507.9 ft) and a diameter of 40.6 cm (16.0 in). Infiltration into the shaft presents another problem to be considered in the design of the sealing system. Natural groundwaters, in particular aquifers, may exert hydrostatic pressure greater than integral pressure of the Deep Shaft and result in a flow into the shaft. The inherent quality of the high-grade steel shaft coupled with the reinforcing qualities of concrete should adequately provide a barrier impervious to leakage in both directions.

The design of this unique bioreactor incorporates state-of-the-art drilling procedures currently practiced by water well and oil well drillers all over the world. The final considerations for drilling methodology and construction materials ultimately depend on geology of the site. Shaft drilling technology is not new and correct procedures can be documented at well sites throughout the world.

Flow Process Description

Figure 42 is a schematic diagram of the Deep Shaft plant flow. Flow from the industries and the town of Paris enters the conventional MOE plant and is subjected to primary treatment, which consists of coarse screening and degritting. After pretreatment, ferric chloride is added at a wet well for phosphorus removal, and the influent is pumped to a splitter box where part of the flow is drawn off to feed the Deep Shaft facility. Alkaline pH is neutralized by acid addition, and continuous flow to the shaft is assured by a surge tank. The flow from the surge tank is introduced into the shaft at the top of a vertical tube (downcomer) which extends to the bottom of the shaft. The flow then returns to the surface in the annular section (riser) between the downcomer pipe and the shaft casing. The shaft contents are cycled several times as a portion of the flow is discharged by gravity to the flotation tank. A chemical flotation aid is added to the flotation tank influent to improve suspended solids removal. After solids separation, the treated effluent


SEWAGE
POLYMER
AIR
AIR
EFFLUENT
LEGEND
FI FLOW INDICATOR
FA FLOW ALARM
FS FLOW SWITCH
FRC FLOW RECORDER CONTROLLER

STREAM NO.	STREAM DESCRIPTION ◆
1	SEWAGE
2	AIR FLOW
3	POLYMER FEED
4	POLYMER MAKE-UP WATER
5	FLOAT RECYCLE
6	SINK RECYCLE
7	WASTE FLOAT
8	EFFLUENT
9	POLYMER
10	FLOTATION FEED
11	DILUTION WATER

EQUIPMENT NO.	EQUIPMENT DESCRIPTION ●
1	AIR COMPRESSOR
2	STANDBY AIR COMPRESSOR
3	ROTAMETER
4	AIR INJECTION PIPING
5	DEEP SHAFT
6	SINK RETURN PUMPS
7	FLOTATION TANK
8	FOAM BREAKERS
9	SLUDGE STORAGE
10	PARSHALL FLUME
11	POLYMER FEED TANK
12	POLYMER MAKEUP TANK
13	POLYMER FEED PUMP
14	STANDBY POLYMER FEED PUMP
15	SURGE TANK

Figure 42. Paris, Ontario Deep Shaft flow diagram.

Activated sludge is recycled from the flotation tank to the shaft to maintain the bacteria population, and air is injected into the downcomer to ensure viability of the bacteria and to provide impetus for circulation (Figure 42). At the head of the shaft, spent air is exhausted to the atmosphere from a head tank. After the addition of the polymer, flow from the shaft is directed to a flotation tank where the solids are removed The treated effluent then passes over a weir and to disposal as final effluent.

To start the wastewater circulating, compressed air is injected at a fraction of the depth in the riser. The rising bubbles induce an upward flow in the liquid column, and because the average weight of water in the downcomer is greater than the average weight of water in the riser, circulation begins. Once circulation is established, air injection is gradually transferred to the same depth in the downcomer pipe. On larger shafts eventually all of the air will be injected into the downcomer pipe. Because of the downward velocity of the liquid, 7.6 to 12.7 cm/sec (3.0 to 5.0 in/sec), and the natural rise velocity of the air bubbles, 1.93 cm/sec (0.76 in/sec) the air is drawn down the shaft with the liquid. As the air passes into the riser, the expanding bubbles drive the flow upwards before escaping into the atmosphere, thus maintaining the circulation.

At a velocity of 12.7 cm/second (5.0 ft/sec) the effluent takes between 3 to 6 minutes to complete each circuit. This longer-than-usual contact time for each air bubble enables the bacteria colony to make optimum use of the available oxygen and partly explains the high oxygen transfer efficiency.

Theories involving the cycling environment of the shaft can be used to explain lower sludge production in the Deep Shaft. As influent proceeds down the downcomer, the resulting increase in hydrostatic pressure results in a substantial increase in oxygen solubilities. The resulting substrated uptake is a function of metabolism rather than other physicochemical limiting factors. The Deep Shaft cycling environment of rapidly changing hydrostatic pressure exerts extreme physiological stresses on the microbiota resulting in a significant reduction in the production of biomass. Energy from the enzymatic sequences normally used in cellular growth and reproduction is shunted off into coping with the abnormal stresses created by the cycling environment of the Deep Shaft. Sludge production in the Deep Shaft facilities is 0.25 to 0.50 kg (0.6 to 1.1 lb) of sludge produced for each kilogram of BOD removed.

The solids separation phase of the process utilizes dissolved air bubbling out of solution in the riser to form a sludge blanket floating on top of the flotation tank. This sludge blanket is formed by the particles suspended in the rising waste adhering to the small air bubbles. A polymer aid is added to the waste as it leaves the Deep Shaft to encourage solids separation. The polymer forms a bridging chain which agglomerates the individual solid particles and results in a more buoyant floc being produced in the flotation tank.

The advantage to this flotation system is that both settled and floated sludges are returned rapidly to the shaft and mixed with new influent wastes. This is beneficial for an activated sludge process. Sludge concentrations of 6 to 10 percent are indicative of luxury thickening in the flotation tank.

The increase is useable oxygen deliverability and higher solids concentration in the shaft can result in an aeration volume reduction of 50 times that of conventional systems. However, it should be noted that it can cost 10 to 20 times more per unit volume to install a subsurface Deep Shaft aeration system rather than an overground structure.

The ICI Deep Shaft aeration process is a high rate process. Retention times for conventional activated sludge plants treating a similar flow are usually in the range of 6 to 12 hours or longer. The Deep Shaft aeration process retention time of approximately one hour (depending upon the waste) is substantially shorter due to a combination of factors, including:

- Optimized oxygen intensity
- Efficient utilization of an inexpensive source of oxygen
- Greatly enhanced contact time
- Enhanced mass transfer due to improved oxygen solubility
- Ability to operate at high solids level in the shaft
- Excellent mixing.

Another advantage of suspended solids removal using flotation tanks is that both solids separation and sludge thickening is performed in one process resulting in a denser sludge. The solids content of sludge produced from the flotation tank is about 7 to 10 percent, whereas a conventional activated sludge plant may produce a sludge of 1.5 percent solids. The solids concentration generated in the flotation tank will vary depending upon the nature of the substrate but generally appears to be much more concentrated than in conventional sedimentation systems.

OPERATIONAL INFORMATION

Operational monitoring of the Deep Shaft facility consists of a number of parameters. Figures 43 and 44, copies of the Paris data sheets, show the exact operational parameters recorded daily.

The influent into the plant is monitored for flow, temperature, surface tension, suspended solids, color, and odor. The in-line operation monitoring consists of volatile mixed liquor suspended solids (MVLSS), pH, dissolved oxygen, respiration, temperature, and settleable solids pressure in the shaft.

The polymer feed system consists of 1.2 m^3 make-up tank on line to a 2.3 m^3 feed tank. An 0.4 percent solution of polymer (Praestol 423K) is made up every third day. Mixing is accomplished using a polyethylene tank outfitted with a 1-horsepower mixer (350 rpm). The batch is stirred for 45 minutes and then transferred to the polymer feed tank which is sized for a three-day supply of the aqueous polymer solution. The polymer is then fed into the exit of the head tank. The polymer feed flow is automatic and is regulated by a device located at the Parshall flume. This device emits a sonic signal which regulates the volume of polymer added to the waste stream. The principal of this automated system is the integral relationship of sonic signal and polymer concentration.

Sulfuric acid stored in a 1.2 m^3 tank is used for pH balancing. The generally alkaline nature of the waste stream originates with the industrial contribution. The feed of the concentrated acid, on the average, is 20 mℓ/min and is sufficient to maintain the pH around 7.

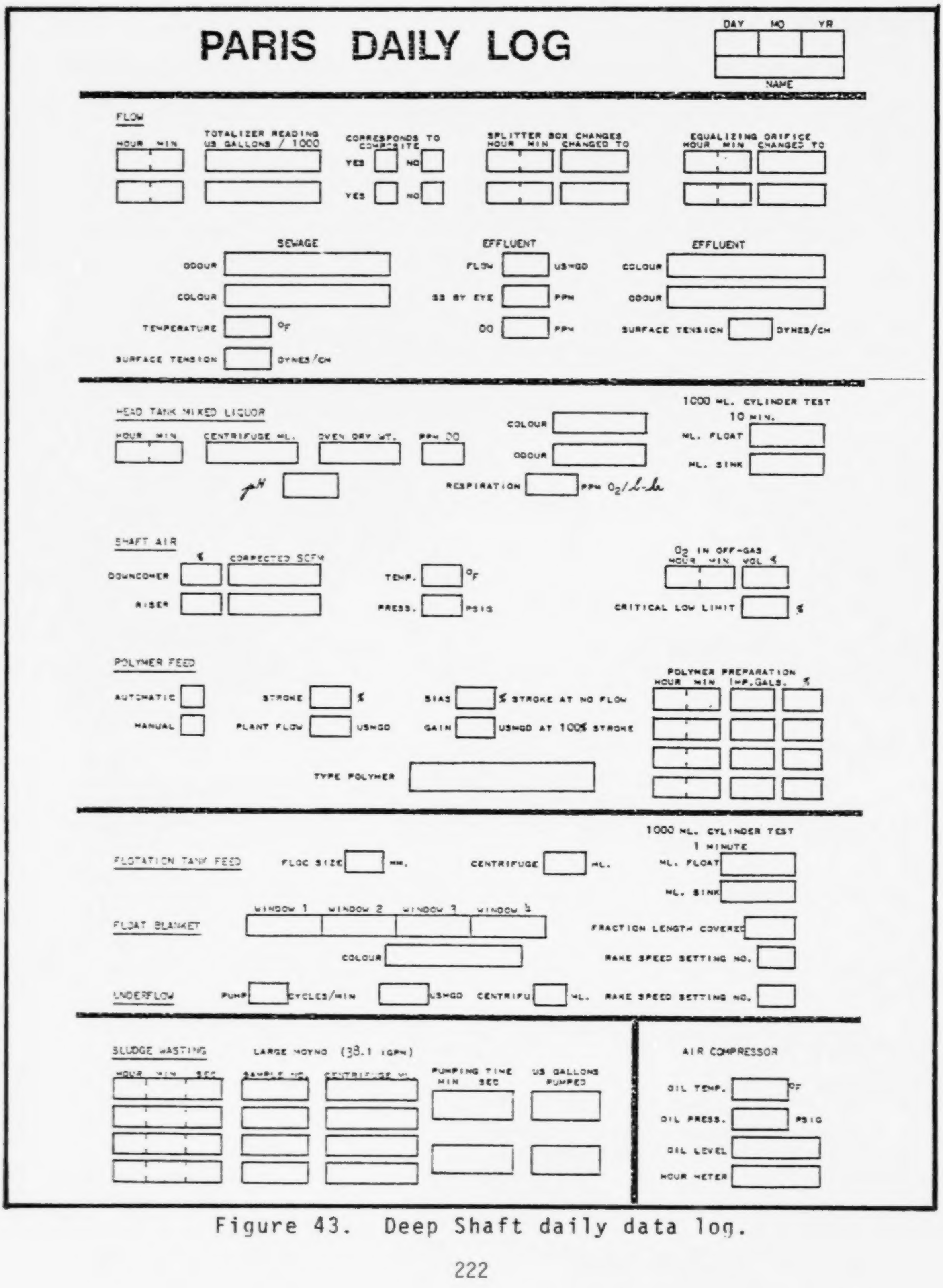
Depending on the MLVSS concentration in the Deep Shaft, sludge is wasted in order to maintain the optimal concentrations to yield maximum BOD and COD reduction.

At present, the Deep Shaft has a designed treatment capacity of 1.9×10^3 m^3/day (0.5 MGD). However, the limiting operation factor is the flotation tank. The designed capacity of this unit is approximately 4.7×10^3 m^3/day (1.2 MGD); therefore, the solid-separation capacities of these facilities would have to be increased to allow for increased waste flows.

Operational Advantages of the Deep Shaft Process

Low Capital Cost--

The ICI Deep Shaft Process is expected to cost at least 20 percent less than rival mechanical systems. This depends, of course, upon ease of shaft drilling and raw waste characteristics.



PARIS DAILY LOG

DAY MO YR

NAME

FLOW

HOUR MIN

TOTALIZER READING US GALLONS / 1000

CORRESPONDS TO COMPOSITE

YES ☐ NO ☐

YES ☐ NO ☐

SPLITTER BOX CHANGES HOUR MIN CHANGED TO

EQUALIZING ORIFICE HOUR MIN CHANGED TO

SEWAGE

ODOUR

COLOUR

TEMPERATURE °F

SURFACE TENSION DYNES/CM

EFFLUENT

FLOW USMGD

SS BY EYE PPM

DO PPM

EFFLUENT

COLOUR

ODOUR

SURFACE TENSION DYNES/CM

HEAD TANK MIXED LIQUOR

HOUR MIN

CENTRIFUGE ML.

OVEN DRY WT.

PPM DO

pH

COLOUR

ODOUR

RESPIRATION PPM O_2/l-hr

1000 ML. CYLINDER TEST
10 MIN.

ML. FLOAT

ML. SINK

SHAFT AIR

% CORRECTED SCFM

DOWNCOMER

RISER

TEMP. °F

PRESS. PSIG

O_2 IN OFF-GAS
HOUR MIN VOL %

CRITICAL LOW LIMIT %

POLYMER FEED

AUTOMATIC ☐

MANUAL ☐

STROKE %

PLANT FLOW USMGD

BIAS % STROKE AT NO FLOW

GAIN USMGD AT 100% STROKE

TYPE POLYMER

POLYMER PREPARATION
HOUR MIN IMP.GALS. %

FLOTATION TANK FEED

FLOC SIZE MM.

CENTRIFUGE ML.

1000 ML. CYLINDER TEST
1 MINUTE

ML. FLOAT

ML. SINK

FLOAT BLANKET

WINDOW 1 WINDOW 2 WINDOW 3 WINDOW 4

COLOUR

FRACTION LENGTH COVERED

RAKE SPEED SETTING NO.

UNDERFLOW

PUMP CYCLES/MIN

USMGD

CENTRIFU ML.

RAKE SPEED SETTING NO.

SLUDGE WASTING

LARGE MOYNO (38.1 IGPM)

HOUR MIN SEC

SAMPLE NO.

CENTRIFUGE ML.

PUMPING TIME MIN SEC

US GALLONS PUMPED

AIR COMPRESSOR

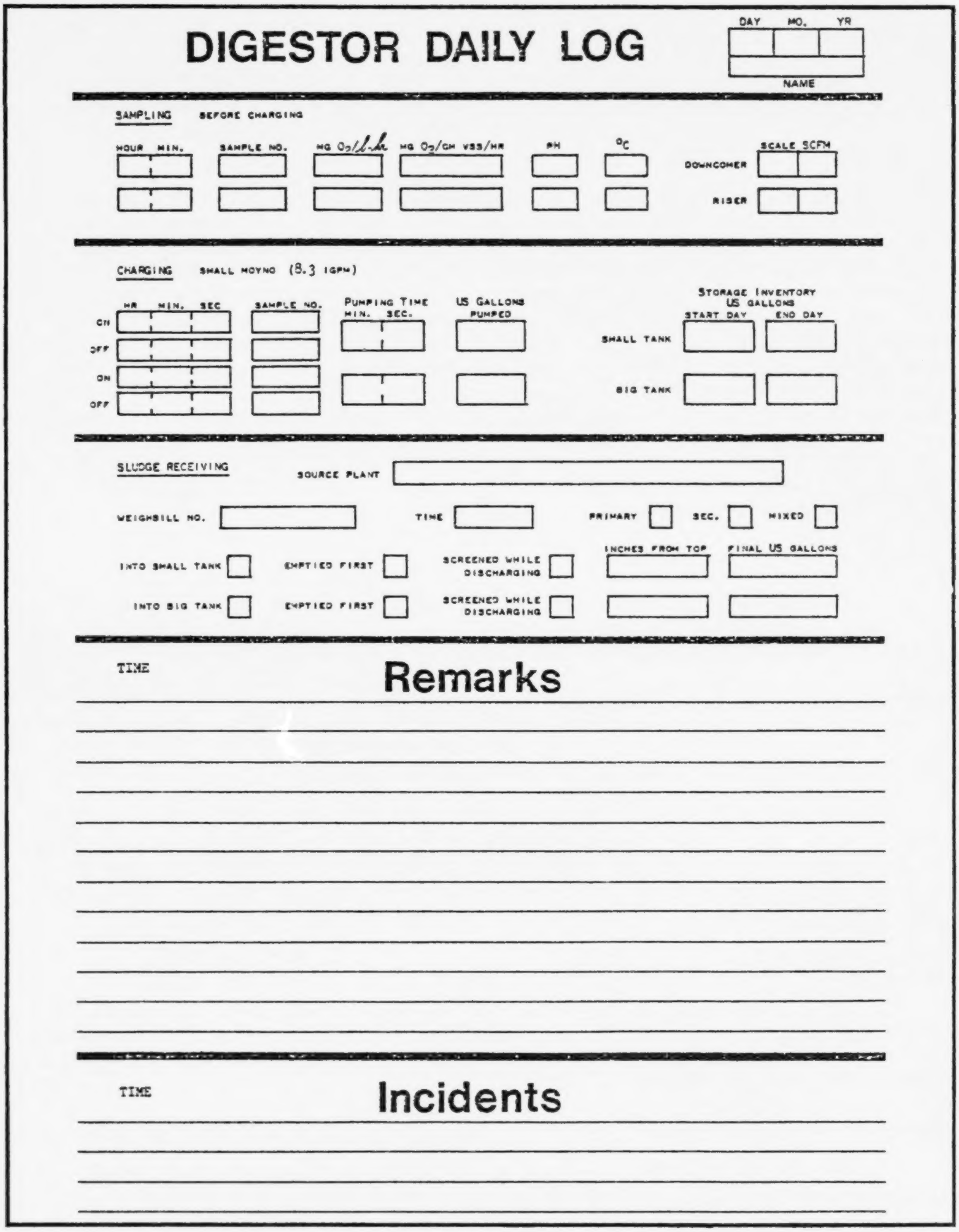
OIL TEMP. °F

OIL PRESS. PSIG

OIL LEVEL

HOUR METER

Figure 43. Deep Shaft daily data log.



DIGESTOR DAILY LOG

DAY	MO.	YR

NAME

SAMPLING BEFORE CHARGING

HOUR MIN.	SAMPLE NO.	MG O_2/l-hr	MG O_2/GM VSS/HR	PH	°C

	SCALE SCFM
DOWNCOMER	
RISER	

CHARGING SMALL MOYNO (8.3 IGPM)

	HR MIN. SEC	SAMPLE NO.	PUMPING TIME MIN. SEC.	US GALLONS PUMPED
ON				
OFF				
ON				
OFF				

STORAGE INVENTORY US GALLONS

	START DAY	END DAY
SMALL TANK		
BIG TANK		

SLUDGE RECEIVING SOURCE PLANT

WEIGHBILL NO. TIME PRIMARY ☐ SEC. ☐ MIXED ☐

				INCHES FROM TOP	FINAL US GALLONS
INTO SMALL TANK ☐	EMPTIED FIRST ☐	SCREENED WHILE DISCHARGING ☐			
INTO BIG TANK ☐	EMPTIED FIRST ☐	SCREENED WHILE DISCHARGING ☐			

TIME

Remarks

TIME

Incidents

Figure 44. Deep Shaft daily digestor data log.

Reductions in surface area requirements for the sewage treatment plant as typified by the ICI Deep Shaft Process should offer additional savings associated with land acquisition. Advantages of enclosing the treatment facility may also be easily realized.

Low Temperature Operation --

Successful operation of waste treatment facilities at low ambient conditions is imperative in northern latitudes. The logistics of building the biological aeration unit underground and the configuration of the unit allows the system to be entirely enclosed ensuring good bioreactor temperature control. An enclosed structure offers favorable working conditions all year round. It was found that an enclosed system is easier to maintain and is likely to receive better attention, especially in the winter months. The wastewater temperature will not drop below the influent temperature, as the influent by the nature of the process is not exposed to ambient conditions. Biological activity is not impaired, as the influent is never exposed to ambient conditions, which result in a temperature reduction and consequent reduction in biological activity.

Absence of Obnoxious Odor--

The absence of obnoxious odor is important from an aesthetic and operations standpoint. The enclosed subsurface nature and highly aerobic environment in the Deep Shaft Process results in a facility free from obnoxious odors. The gaseous carbon dioxide generated is vented to the atmosphere directly from the head tank. This results in a safe working environment.

Minimization of Plant Surface Area--

Minimization of plant surface area is critical to ensure the lowest possible civil and building costs. The small surface area requirements associated with Deep Shaft results in lower foundation cost and allows the enclosure of the entire plant to be considered without incurring large costs.

Competitive Operating Costs--

The annual operating cost of the ICI Deep Shaft Process is expected to be competitive with most other systems. The polymer costs are expected to be offset by aeration horsepower savings. particularly in larger plants.

Ease of Operation--

The waste treatment process must be very easy to operate and must offer a large degree of reliability since the process will be expected to operate on a semi-attended basis by operators who may not be technically trained in sewage treatment plant operation. There are no sophisticated process controls involved in the operation of Deep Shaft technology. The process is designed to be operated by personnel with no previous experience in wastewater treatment and with no special technical skills.

Alarm systems can be included not only to announce shutdown of operating compressors but also start-up of standby units automatically. Polymer addition equipment also features liquid level alarms indicating failure of polymer feed pumps.

Operator responsibilities include periodic sludge wastage, polymer mixing and routine maintenance of the compression system plus maintenance of the rakes on the flotation cells. A Parshall flume is used to measure effluent flow, and a sonic signal is relayed to the chemical flotation aid feed equipment to ensure proper amounts of chemical flotation aid are added.

Process reliability in the Deep Shaft is enhanced by the large oxygen deliverability and turbulence in the aeration shaft which results in a capability to buffer BOD_5 and pH shock loads. Filamentous organisms can cause severe bulking problems in conventional biological processes. However, filamentous organisms can exist in the highly aerobic Deep Shaft; they do not appear to pose the problems associated with solids separation in conventional systems. Because of the extensive turbulence, morphology of the filamentous organisms is greatly changed as they pass through the shaft.

Sludge Handling and Disposal--

Sludge handling and disposal costs account for approximately 50 percent of the cost of operating a sewage treatment plant. The ICI Deep Shaft flotation cell produces a solids float of 7 to 10 percent, stabilized by an innovative aerobic digestor.

Tests performed by ICI at Billingham, England, have shown that sludge taken from the ICI Deep Shaft process has a specific lower resistance to dewatering. At the Paris plant, this is expected to be further enhanced because of chemicals used to improve bubble attachment in the flotation cell.

TREATMENT EFFICIENCY

The Paris Deep Shaft Facility has just recently become operational. The amount of waste data thus far generated is, therefore, limited. The in-house monitoring program is also limited in scope. Table 80 shows the influent and effluent quality monitored during weekends for a three month period, March to July 1977; Table 81 shows the daily effluent monitoring data for May 1977. Tables 82, 83, and 84 relate the removal efficiencies for the parameters being monitored. The removal efficiencies in

TABLE 80

DEEP SHAFT FACILITY: PARIS, ONTARIO

WEEKEND OPERATION

(March 4 - July 15, 1977)

INLET	AVERAGE (ppm)	RANGE (ppm)	DATA POINTS /39 (days)
BOD_5	105	57 - 262	30
$SBOD_5$	24	9 - 96	30
Whole COD	356	204 - 1264	18
TSS	207	102 - 726	30

OUTLET	AVERAGE (ppm)	RANGE (ppm)	DATA POINTS /39 (days)
BOD_5	13	5 - 33	33
$SBOD_5$	7	1 - 26	32
Whole COD	42	25 - 94	22
TSS	18	10 - 32	33

TABLE 31. DEEP SHAFT FACILITY, PARIS, ONTARIO: MAY 1977 EFFLUENT MONITORING DATA (mg/ℓ)

Day	SS	BOD_5	Soluble BOD_5	COD
1	18	11	8	42
2	32	32	22	
3				
4	Laboratory technician ill			
5				
6	19	18	10	53
7	16	19	9	37
8	21	13	8	37
9	34		24	109
10	38	58	50	130
11	52	56	39	121
12	94	85	43	135
13	29	23	12	76
14	14	15	4	50
15	14	12	10	52
16	38	34	25	111
17	37	32	19	97
18	47	38	24	102
19	30	35	21	127
20	32	19	6	62
21	19	11	5	42
22	22	11	7	20
23	19	11	9	45
24	49	40	22	111
25	23	22	14	74
26	42	39	24	102
27	28	24	12	79
28	17	9	6	37
29	17	8	7	29
30	30	31	19	63
31	45	42	-	112
Total	876	748	459	2,055
Average	31	27.7	17	76
Corrected average	25.0	20.4	12.7	66

TABLE 92. BOD REMOVAL EFFICIENCY

Day	Influent concentrations influent BOD_5 (mg/ℓ)	Effluent concentrations BOD_5 (mg/ℓ) out	Kg (lb) BOD loaded	Kg (lb) BOD removed	Removal efficiency* (%)
			flow = 473 m^3/day (0.12 MGD)		
1	90	11	43 (94.8)	37 (82)	87.7
2	195	32	92 (202.9)	77 (170)	83.6
3	†				
4					
5					
6	116	18	55 (121)	46 (101)	83.6
7					
8					
9					
10	180	58	85 (187)	58 (128)	67.8
11	224	56	106 (234)	79 (174)	75.0
12	204	85	97 (214)	56 (123)	58.3
13					
14	141	15	67 (148)	60 (132)	89.4
15	116	12	55 (121)	49 (108)	89.6
16	195	34	92 (203)	76 (168)	82.6
17	169	32	80 (176)	65 (143)	81.1
18	180	38	85 (187)	67 (148)	78.9
19	213	35	101 (223)	84 (185)	83.6
20	102	19	48 (106)	39 (86)	81.4
21	107	11	51 (112)	45 (99)	89.7
22	102	11	48 (106)	43 (95)	89.2
23	113	11	53 (117)	48 (106)	90.3
24	160	40	76 (168)	57 (126)	75.0
25	167	22	79 (174)	69 (152)	86.8
26	202	39	96 (212)	77 (170)	80.7
27					
28					
29					
30	262	31	124 (273)	109 (240)	88.2
31	204	42	97 (219)	77 (170)	79.4

* Average BOD_5 removal efficiency based on the record data for the month of May 1977 is 81.9%.

† Blank section in recorded data is due to sampler and power failure.

TABLE 83. COD REMOVAL EFFICIENCY

Day	Influent concentrations influent COD (mg/ℓ)	Effluent concentrations COD (mg/ℓ)	Kg (lb) COD loaded flow = 473 m^3/day (0.12 MGD)	Kg (lb) COD removed flow = 473 m^3/day (0.12 MGD)	Removal efficiency* (%)
1	238	42	113 (249)	93	82.4
2	†				
3					
4					
5					
6					
7					
8					
9	565	109	267 (589)	216 (476)	80.7
10	531	130	251 (553)	190 (419)	75.5
11	805	121	381 (840)	324 (714)	85.0
12	610	135	287 (633)	225 (496)	77.9
13	479	76	227 (500)	191 (421)	84.1
14	418	50	198 (437)	174 (384)	88.0
15	410	52	194 (428)	169 (373)	87.3
16	652	111	308 (679)	256 (564)	83.0
17	507	97	240 (529)	194 (428)	80.9
18	579	102	274 (604)	226 (498)	82.4
19	698	127	330 (728)		81.8
20					
21	307	42	145 (320)	125 (276)	86.3
22	224	20	106 (234)	97 (214)	91.1
23	513	45	243 (536)	221 (487)	91.2
24	702	111	332 (732)	280 (617)	84.2
25	582	74	275 (606)	240 (529)	87.3
26	618	102	292 (644)	244 (538)	83.5
27					
28					
29					
30					
31	604	112	286	234	81.5

* Average COD removal efficiency based on the recorded data for the month of May 1977 is 83.9%.

† Blank section in record data is due to sampler and power failure.

TABLE 84. SUSPENDED SOLIDS REMOVAL EFFICIENCY

Day	Influent S S (mg/ℓ)	Effluent S S (mg/ℓ)	Removal efficiency (%) *
1	124	18	85.5
2	194	32	83.5
3	†		
4			
5			
6	209	19	90.9
7			
8			
9	229	34	85.2
10	182	38	79.1
11	291	52	82.1
12	218	94	56.9
13	226	29	87.2
14	193	14	92.7
15	176	14	92.0
16	314	38	86.8
17	191	37	80.6
18	233	47	79.8
19	208	30	85.6
20	219	32	85.3
21	177	19	89.3
22	139	22	84.2
23	117	19	83.7
24	208	49	76.4
25	270	23	91.5
26	203	42	79.3
27			
28			
29			
30			
31	209	45	78.5

* Average suspended solid removal efficiency is 83.5%

† Blank section in the recorded data is due to sampler and power failures.

general are in the low 80 percent range for BOD, COD, and suspended solids. At first glance, these results seem low when compared to treatment efficiencies of conventional activated sludge systems for industrial wastes. The somewhat low values of removal efficiency can be attributed to the highly fluctuating influent characteristics of the textile manufacturer.

Effects of Wastes on the Receiving Biota

At the Paris plant, sludge was introduced from the on site conventional S.T.P. It was assumed that its biota would be acclimated to the type of industrial/municipal wastewater it would be treating. It was found that the biota quickly adapted to the pressure cycling in the Deep Shaft Process. In addition, there were no problems experienced by the microorganism functioning with BOD reductions, and flocculation characteristics generally stabilized within 24 hours. In general, the microbiological populations in the Deep Shaft sewage treatment system have been found to be very similar to those of the conventional activated sludge systems. The effects of dilution on the receiving microbiological population have been favorable. Any potentially toxic compounds inherent in the waste stream seem to be diluted to a concentration with minimal deleterious effects on biotic populations. However, this says little about the effect of the eventual biomagnification of toxic or carcinogenic substances which might be present in the treatment plant effluent.

Impact on Sludge Handling

Luxury sludge thickening is an integral part of the solid separation process in the flotation tank. A solids content of 6 to 10 percent is common and occurs without a separate sludge dewatering process. An innovative sludge stabilization system has been implemented at the Paris pilot facility, a 7.6 m (3.0 in) diameter, 152.4 m deep (500 ft), U-tube Deep Shaft aerobic digestor. The operation is entirely experimental, and initial results indicate that this hybrid digestor is capable of stabilizing raw sludge in one-fifth the time of conventional aerobic digestors. Documentation, at present, is not available because presumptive and conclusive testing is not completed.

The impact of these innovative sludge generation and stabilization procedures could be very significant in reducing the operational cost of sludge handling. This unique stabilization process could also have a profound effect on structural cost when related to costs accrued in construction of conventional aerobic digestors. The retention time reduction associated with the Deep Shaft U-tube could reduce the size needed for the structure of conventional anaerobic sludge digestors; wasted sludge from the experimental stabilizer and flotation tank is routed into the headworks of the conventional sewage treatment plant located adjacent to the pilot plant.

ECONOMIC EVALUATION

The Paris Deep Shaft facility was constructed by CIL for an initial cost of $400,000 (based on 1976 cost data). This pilot system was completely financed by ICI. A construction cost summary is shown in Table 85. These costs were derived from estimates supplied to SCS Engineers by Eco Research Ltd. which did not include either the costs associated with the construction of the building which houses the treatment facility or those incurred with site preparation for construction. Estimation of these costs were derived from Means Cost Data, 34th edition, 1976.

The total estimated 1976 operation and maintenance costs for the Deep Shaft Facility are outlined in Table 86. A conservative estimate of maintenance cost was 10 percent of total construction cost. This relatively small maintenance cost is due, in part, to the inherent reduced land requirement of this facility. Operation labor and supervision were based upon a staff of one supervisor and one laborer. Cost of chemicals usage was based on $3.50/kg ($350/lb) for the polymer supplied by Bayer Chemical Company and $0.04/ℓ ($0.04/gal) for sulfuric acid (price quote by McKesson Chemical Company, 1976). Power costs were based on the total horsepower utilized by the Paris pilot facility. The sludge disposal costs were not included, since this facility recirculates wasted sludge into the headworks of the MOE conventional wastewater treatment facility.

The cost of BOD and COD removal is relatively high. The small volume of wastes being treated and the experimental nature of the pilot plant facility are major factors contributing to this elevated cost. A removal cost comparison between this facility and large scale conventional industrial systems is not applicable.

TABLE 85. PARIS, ONTARIO DEEP SHAFT FACILITY: ESTIMATED CONSTRUCTION COST SUMMARY

	Capital investment	Cost
[*] 1.	Hardware - installation (includes): a. Air compressor system (2) b. Sink return pumps c. Flotation tank d. Foam breakers e. Parshall flume f. Polymer feed tank g. Polymer make-up tank h. Polymer feed pump (2) i. Rotometer j. Deep shaft k. Surge tank l. Acid tank m. Instrumentation	$ 283,000
[†] 2.	Building construction - based on 15 x 15 m dimension at $270.00/m^2	63,000
[†] 3.	Site preparation	54,000
	Total costs	$ 400,000

[*] Determined from cost estimates supplied Eco Research Ltd. Based on 1976 cost.

[†] Building construction cost and site preparation cost was estimated from Building Construction Costs data 1976, 34th edition.

TABLE 86. PARIS, ONTARIO DEEP SHAFT FACILITY: O&M COST 1976

	Costs/yr
• Operating labor and supervision*	$ 15,000
• Chemicals - acid (H_2SO_4 at $0.038/gal)	400
polymer (Prerestol - 423K @$3.50/kg)	4,000
• Power (compressor + pump hp)	200
• Maintenance (1% of construction)	4,000
• Miscellaneous supplies	1,000
• Amortize investment† (20 yrs at 6%)	35,000
Total	$ 59,600

Cost of kg BOD removed = $2.60/kg ($2.60/lb)
Cost of kg COD removed = $0.70/kg ($0.70/lb)

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[*] It should be noted that the Deep Shaft Facility does not require continuous personnel monitoring.

[†] Capital recovery factor = 0.08718. Salvage value not included.

AN EASTERN CHEMICAL
PRODUCTION PLANT UNOX FACILITY

INTRODUCTION

In 1946, a 5.68 x 10^3 m^3day (1.50 MGD) secondary wastewater treatment plant was constructed on the grounds of an East Coast chemical company. Initial secondary treatment processes consisting of trickling filters and activated sludge eventually produced sufficient odors to cause citizen complaints. Consequently, in 1972, the company installed a UNOX pure-oxygen, biological system to handle secondary treatment of the influent waste streams.

Waste streams at the plant are from two sources: 1) sanitary wastes; and 2) industrial wastes. The treatment plant occupies approximately 1 ha (2.5 ac) of land and treats between 4.9 to 5.7 x 10^3 m^3/day (1.3 and 1.5 MGD). Total hydraulic retention time available in the UNOX system is 12.7 hours. The biological treatment system is aerobic.

Various problems are encountered in conventional biological treatment of industrial wastes containing highly carbonaceous and proteinaceous wastewaters. Such difficulties include:

- Varying quantity and quality of organic wastewater influent to the treatment plant (discharged from a large chemical complex), resulting in non-equilibrium conditions

- Synthetic organic constituents inhibitory to nitrophilic protozoa and flocculating organisms

- Surfactants causing foaming problems.

To assist in the elimination of potential problems, the designers of the UNOX facility proposed a system with sufficient volume and suitable hydraulic retention time. Since this system has to meet a BOD and suspended solids effluent amenable to further municipal treatment, the primary concern of the treatment facility is a significant reduction,on an odor-free basis, of the BOD and suspended solids in the effluent. Consequently, pure oxygen is used in the UNOX system to reduce large quantities of organic waste loads and maintain an equilibrium condition through the system.

Plant History

In April 1972, the chemical plant began operation of the UNOX process. Before installation of the system, the treatment plant consisted of primary and secondary treatment with trickling filters and an activated sludge unit. Odors arising from the trickling filter prompted neighboring citizens to complain. Consequently, the chemical company sought a treatment system which would eliminate the odor as well as reduce the BOD and suspended solids (SS) that were discharged.

The effluent from the chemical plant enters a municipal sewerage system and is further treated at the municipal wastewater treatment plant. Consequently, effluent quality has to meet the upper limits of BOD of 250 parts per million (ppm) and suspended solids of 250 ppm. If these criteria are exceeded on an annual average, the municipality charges the chemical company an extra 3.3 cents per kilogram of BOD.

The UNOX system was considered for the treatment of the combined sanitary and industrial waste because it could treat the wastewaters sufficiently. In addition, a cover on the UNOX treatment system eliminates the odor problem.

The company has been pleased with the cost of operation and maintenance of the system.

Site Location and Regional Characteristics

The chemical plant, like many others located in the eastern part of the United States, is nestled in a residential and commercial area and provides a major source of employment for the area. These plants generally are located in cities with population of 10,000 to 20,000 people. Consequently these companies considerably impact the communities' economy.

The plant is located in a warm temperate climate with moderate precipitation throughout the four seasons.

WASTEWATER IDENTIFICATION

Waste Sources

The major sources of industrial wastes at the chemical plant are: fermentation processes, biological and natural extraction processes, chemical synthesis processes, formulation processes, research, and sanitary wastes. Discharges from the research contribute a variety of wastes originating from laboratory experimental conditions and quality control. The more common industrial waste discharged into the plant sewerage is the spent broth from antibiotic manufacturing.

Other discharges considered wastewaters include once-through cooling water, recirculated water and broiler blowdown. These wastewaters are released to waterways and thus are controlled under the National Pollution Discharge Elimination System Act. The pond system from which most of these discharges flow has been revised for use as a spill collection device to prevent accidental contamination of one of the waterways.

The electrical maintenance program of the plant specifies that transformers containing PCB compounds be sent to outside contractors for repair or disposal. Waste solvent-containing aqueous streams from refining, recrystallization or crystal washing operations are sent to solvent recovery units, and concentrations of solvents in the still waste and cleanup operations are limited by policy. Monitoring of these streams by gas/liquid chromatography methods is mandated. Some small volume solvents are shipped out of the plant for recovery by a contractor.

Occasional contaminated fermentor batches are either dumped slowly into the sewer or are trucked to the treatment plant where they are pumped into one train of the UNOX system, and held until the BOD value is low enough to warrant passing the mixed liquor back into the system. Either of these procedures is carried out only after notification of and by permission of the plant supervisor.

Sequential variations of production and product mix have had no long lasting nor unfavorable effects on the treatment plant, except for such factors as primary solids removal (which is dependent mostly upon the type of influent solids), foaming, at the secondary stage, and physical effects such as line restrictions or blockage. Specifically, the following areas have or have not affected the treatment plant efficiency.

- No problems have been ascribed to toxicity.

- Shock hydraulic loadings have contributed to solids overflow from both the primary and secondary clarifiers during high production periods. This problem has been lessened by the inclusion of surge capacity.

- Organic overload shock has been diminished by prolonged aeration of the overload material, provided it can be isolated and trucked to the treatment plant and the plant design permits isolation of a portion of the secondary treatment system.

- Certain products contribute to foaming, usually substances in the influent rather than substances formed during secondary treatment. Excessive foaming seems to be controlled by water sprays outside the secondary vessel; control inside the vessel does not appear feasible at this time.

- Although not pinpointed to a specific production, the treatment plant did experience for two different, but fairly long lasting periods, filamentous organisms which appeared to dominate the culture. They had little effect on the BOD_5 reduction, but made solids removal difficult because of poor settling and compaction characteristics imparted to the mixed liquor. The cause of growth acceleration of these organisms is unknown. The treatment varied with the lowering of the temperature from the thermophilic to the mesophilic range to eliminate the first condition to the minimizing of dissolved oxygen and deliberate overloading to halt the second condition.

SCHEMATIC AND DESCRIPTION OF SYSTEM

Figure 45 depicts the schematic flow of wastewater through the treatment plant at the chemical processing plant. The UNOX system was based on the design parameters of temperature, pH, BOD, mixed liquor volatile suspended solids (MLVSS), the food to microorganism (F/M) ratio, and the settling characteristics of generated sludge.

The incoming waste load is comprised of industrial waste with a strength of 1,000 to 3,000 mg/ℓ BOD and a flow of 3.8×10^3 m^3/day (1 MGD), and a sanitary waste with a strength of 100 to 300 mg/ℓ and a flow of approximately 1.1×10^3 m^3/day (0.3 MGD). The combined wastes flow to a pump station through a bar screen of 2.5 cm (1.0 in) dia. steel bars approximately 2.5 cm (1.0 in) apart.

Pump Station

The pump station consists of four Demming deep well centrifugal pumps which pump the wastewater and return sludge to a flash mix area where polymer is added. At the pump station, a stationary crane is used to lift the pumps because of a low level 400 KV line above the pump station. The chemical plant has had problems with the pumps. The pump impellors have been picking up calcium from lime and the pumps become unbalanced. These pumps are high maintenance items. From the pump station, the waste influent is pumped to the flash mixer.

Flash Mixer

The flash mixer is comprised of a polymer addition tank where an anionic polymer number (835A magnifloc polymer by American Cyanamid) is added in a concentration of 1 to 2 parts per million

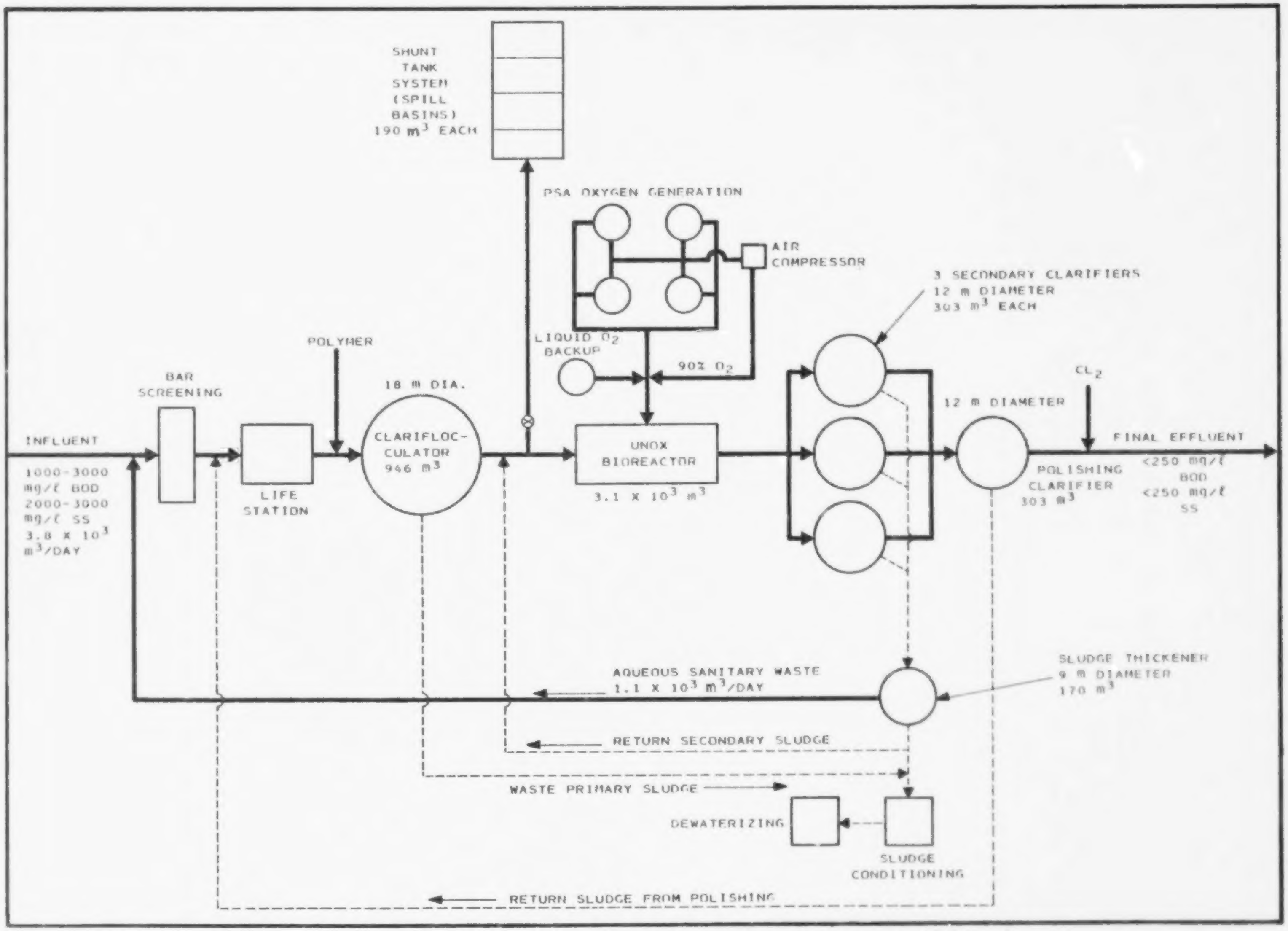

SHUNT TANK SYSTEM (SPILL BASINS) 190 m^3 EACH
PSA OXYGEN GENERATION
AIR COMPRESSOR
3 SECONDARY CLARIFIERS 12 m DIAMETER 303 m^3 EACH
POLYMER
LIQUID O_2 BACKUP
90% O_2
BAR SCREENING
18 m DIA.
12 m DIAMETER
CL_2
INFLUENT
1000-3000 mg/ℓ BOD
2000-3000 mg/ℓ SS
3.8×10^3 m^3/DAY
LIFE STATION
CLARIFLOC-CULATOR 946 m^3
UNOX BIOREACTOR
3.1×10^3 m^3
FINAL EFFLUENT
<250 mg/ℓ BOD
<250 mg/ℓ SS
POLISHING CLARIFIER 303 m^3
AQUEOUS SANITARY WASTE
1.1×10^3 m^3/DAY
SLUDGE THICKENER 9 m DIAMETER 170 m^3
RETURN SECONDARY SLUDGE
WASTE PRIMARY SLUDGE
DEWATERIZING
SLUDGE CONDITIONING
RETURN SLUDGE FROM POLISHING

Figure 45. Schematic of wastewater flow through UNOX plant.

via a flash mixing process. From the polymer addition tank the influent is gravity fed to the clariflocculator.

Clariflocculator

The clariflocculator is manufactured by the Walker Process Equipment Division of Chicago Bridge and Iron Company. The dimensions of the unit are 18.3 m (60.0 ft) diameter, 3.7 to 4.6 m (12 to 15 ft) depth and 946 m^3 (250 gal) capacity. A skimmer rotates around the clariflocculator. The raw primary sludge generated by this primary settling process is taken by Marlow pumps to a sludge conditioning step, followed by vacuum filtration. The effluent from the clariflocculator flows to the UNOX treatment tank where it is joined by the recycled sludge stream containing approximately 1.2 percent mixed liquor suspended solvents (MLSS). Influent wastes that pose a potential explosion hazard are detected by means of two MSA hydrocarbon analyzers located in the first stage, and the stream can be diverted to shunt tanks.

Shunt System

This system has four compartments of 190 m^3 gal (5,000 gal) each which can be used for surge control into the UNOX system. An electrically controlled 45.7 cm gate (Philadelphia Gear Corp. Limitorque) can be activated by a signal from the hydrocarbon analyzer to allow potentially explosive mixtures to flow into the shunt tank for aeration in open tanks. The shunt tank capacity represents a conversion of the old activated sludge system to this storage system in the new plant. The agitators in the four cells of the shunt tank are maintained in a standby condition. The cells are interconnected on the bottom and top and allow the wastewater to be pumped back into the clariflocculator effluent sump which then allows it to flow into the UNOX box.

UNOX System

Figure 46 depicts equipment attached to and incorporated in the 0.3 m (1.0 ft) thick reinforced concrete UNOX box. The UNOX box has a capacity of approximately 3,104 m^3 (820,000 gal) and is approximately 4.3 m (14.0 ft) deep; a 3.0 m (10.0 ft) depth of liquid is maintained, the remaining 1.3 m (4.0 ft) is used for gas.

The oxygen production and supply system used to supply the oxygen for the UNOX process is pressure-swing absorption system (Figure 47). There is an in-depth discussion of the system under "UNOX Treatment System."

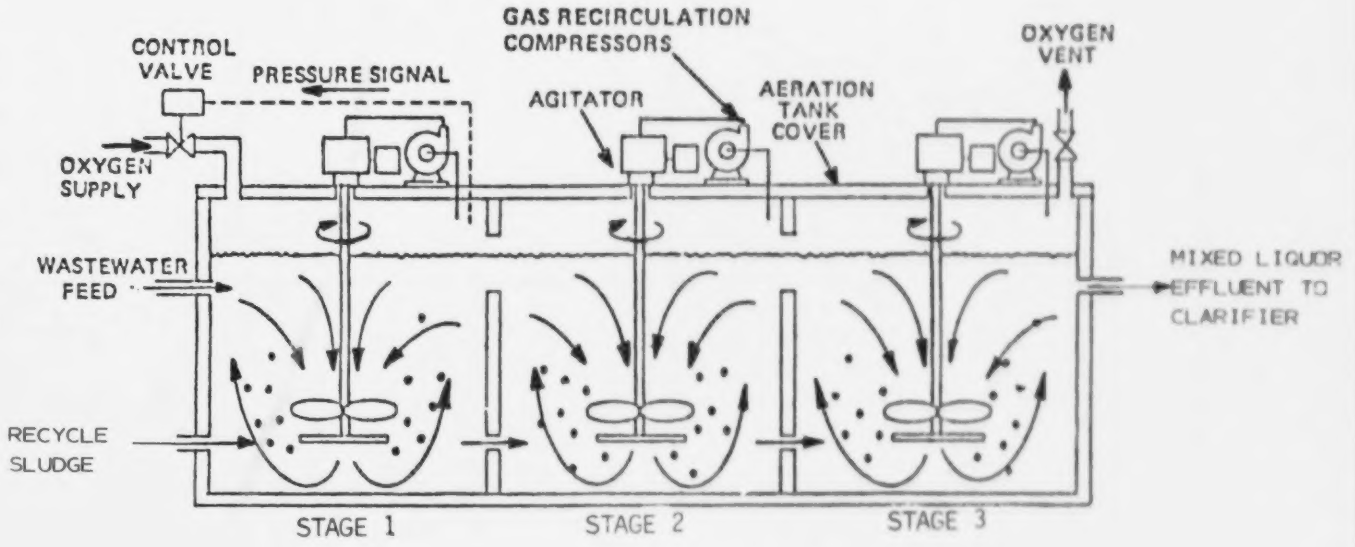
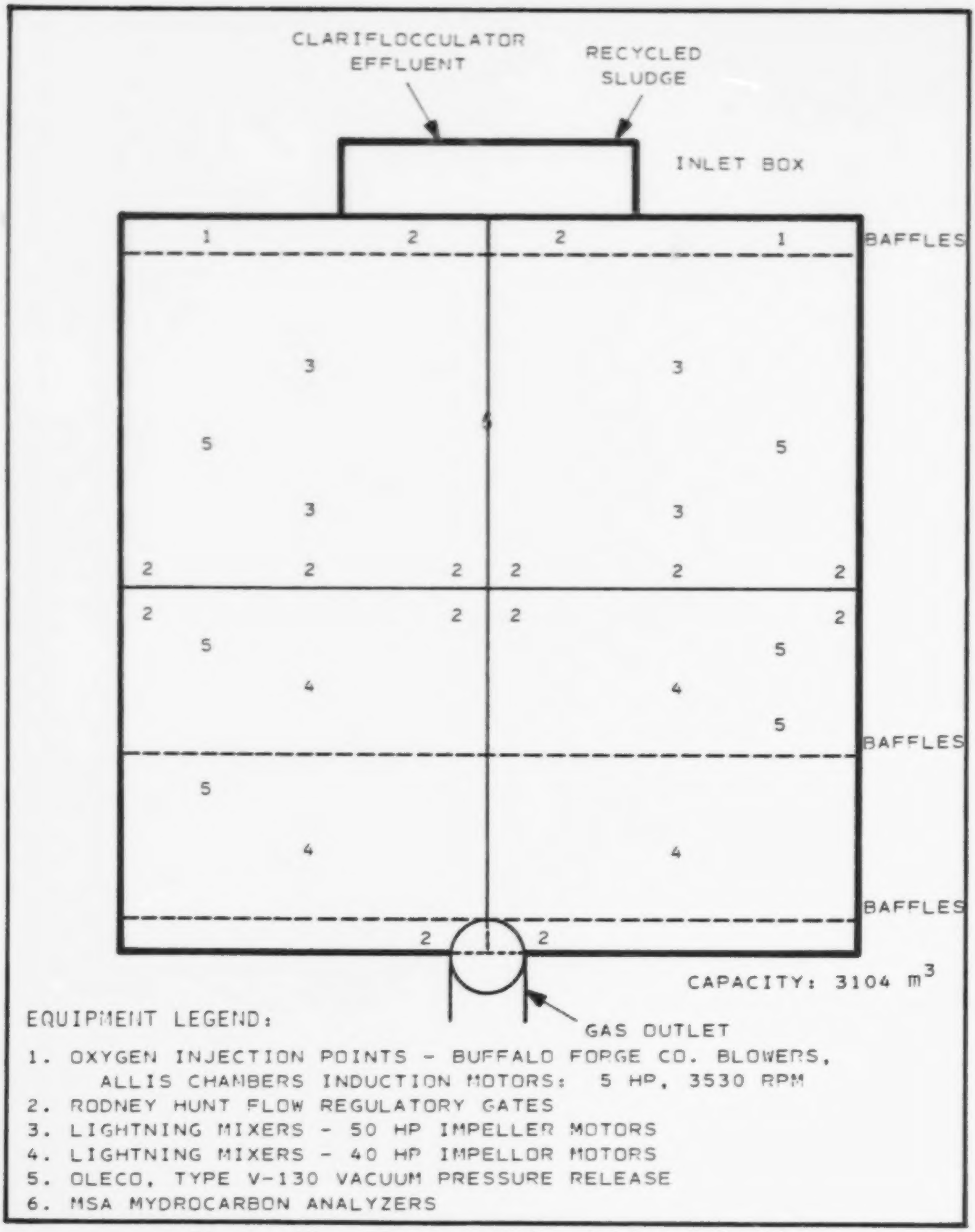

GAS RECIRCULATION COMPRESSORS
CONTROL VALVE
PRESSURE SIGNAL
AGITATOR
AERATION TANK COVER
OXYGEN VENT
OXYGEN SUPPLY
WASTEWATER FEED
MIXED LIQUOR EFFLUENT TO CLARIFIER
RECYCLE SLUDGE
STAGE 1
STAGE 2
STAGE 3

Figure 46. Schematic diagram of UNOX system.


CLARIFLOCCULATOR EFFLUENT
RECYCLED SLUDGE
INLET BOX
BAFFLES
BAFFLES
BAFFLES
CAPACITY: 3104 m^3
GAS OUTLET
1
2
2
1
3
3
5
6
5
3
3
2
2
2
2
2
2
2
2
2
2
5
5
4
4
5
5
4
4
2
2

EQUIPMENT LEGEND:

1. OXYGEN INJECTION POINTS - BUFFALO FORGE CO. BLOWERS, ALLIS CHAMBERS INDUCTION MOTORS: 5 HP, 3530 RPM
2. RODNEY HUNT FLOW REGULATORY GATES
3. LIGHTNING MIXERS - 50 HP IMPELLER MOTORS
4. LIGHTNING MIXERS - 40 HP IMPELLOR MOTORS
5. OLECO, TYPE V-130 VACUUM PRESSURE RELEASE
6. MSA MYDROCARBON ANALYZERS

Figure 47. Flow control and mixing in the UNOX system - overhead view.

Secondary Clarifiers

The effluent from the UNOX box flows into a flow splitter box where the flow is diverted to three 12 m (40.0 ft) diameter secondary, upflow clarifiers each with a capacity of 303 m^3 (80,000 gal). Two-thirds of the UNOX effluent flow from the splitter box enters a manhole which divides the flow by 50 percent for two clarifiers; the other one-third of the flow from the splitter box goes to the third clarifier. The effluent from the clarifiers enters a manhole and is distributed to a final 12 m (40.0 ft), 303 m^3 (80,000 gal) capacity polishing clarifier The effluent from the polishing clarifier is then discharged to the town sewerage system and is further treated in the municipal wastewater treatment plant.

Monitoring Systems

The treatment plant is principally operated by monitoring the Dissolved Oxygen (DO) in the UNOX system on the partial pressure on the walls of the UNOX system. The densitometers are located in the secondary clarifiers and measure the density of the sludge. They are operated on a vibrating tuning fork principal which activates or shuts off a pump depending upon the thickness (density) of the sludge in the secondary clarifiers. The monitoring device controls the recycle of the secondary sludge.

Sludge Handling Facilities

The primary sludge (approximately 12 percent solids) generated from the clariflocculator is pumped by variable speed Marlow pumps to the sludge filtration system. The secondary sludge is pumped from the thickener to the sludge filtration system directly or, preferably, mixed with primary sludge for filtration. Quick lime staked to an 18 percent solution and alum as a 49 percent solution are added to the sludge in the conditioning tank. This process thickens the secondary sludge to about 4.5 percent solids. All the sludge then is processed by vacuum sludge filters. A quantity of 900 to 2,300 kg/day (1,985 to 5,072 lb/day) of quick lime is used and is pumped in a 18 percent slurry by Slugger diaphragm pumps. The alum is pumped by Komline-Sanderson (KS) diaphragm pumps and a BIF piston pump.

Three types of vacuum filters are currently being used - one is a 3 x 3.7 m (10 x 12 ft) KS rotary vacuum filter using stainless steel springs as media. Other vacuum filters are an Amtak clothbelt and a 1.8 x 1.8 m (6.0 x 6.0 ft) Eimco clothbelt. The vacuum pumps are manufactured by Nash. The clothbelts are fastened by Velcro fasteners and are changed weekly. The clothbelts are then washed in a solution of 10ℓ (2.64 gal) of EDTA (SEQUESTRENE). The solution is then heated to 60° C (140°F) for about two hours and allowed to cool down, after which the cloth-belts are washed. Approximately every six weeks, the drums are acid washed using an inhibited hydrocloric acid, trade name Oakite.

The filtrate from the filters is returned to the flash mix tank where the polymer is initially added. On the average, approximately 10 to 12, 3.1 m^3 boxes of wet sludge containing approximately 25 percent solids is disposed every day.

Method of Sludge Disposal

Dewatered waste sludges, including both raw and secondary combined, are disposed of by composting. The combined sludges are collected into dumpster boxes and trucked to a composting area on the plant site. The sludges, sawdust or dried leaves, and animal manures are available, are piled into windrows approximately 1.5 m (5.0 ft) at the base and 1.2 m (4.0 ft) high, but of varying lengths depending upon topography. The windrows are turned daily during the work week for about a month, during which time the temperature goes through thermophilic temperature cycle with a maximum of about 60°C (140°F) and the pH drops to a more neutral range. The individual windrows are then made into a reserve pile which is made available to the public.

Residual cake from the antibiotic production of pharmaceuticals is also composted. In this process, the cake is simply aerated by turning daily with a bucket loader for about a month. The thermophilic cycle is present as with sludge, and the pH ascends to slightly above neutral. This operation takes place on a 2.5 ha (6.18 ac) field in the northwest quadrant of the plant site. The compost is available to the public on a no charge basis, or is disposed by plowing under in successive 10-cm (4.0 in) layers on an adjacent 2.8 ha (7 ac) field, or used as a soil conditioner (as is the sludge compost) on the chemical plant property itself.

Composting has been a means of sludge disposal for over 20 years, but the success of the operation is dependent upon the availability of relatively large amounts of land and an expanding surburban community where willing users are available.

UNOX TREATMENT SYSTEM

The design of the UNOX system is predicated upon pH, COD, and MLVSS and the settling characteristics of the sludge. The system operates at a F/M of about .25 and is based upon advanced, gas-liquid contacting fluid mixing systems design. It is combined with well established air separation and treatment technology, which results in an economical supply of enriched oxygen gas efficiently mixed and dissolved in a mixed liquor of the activated sludge process. Figure 46, a schematic, cross-section of the surface aerator components of the UNOX system, shows how the process works at the treatment plant. The aeration tank is divided into sections or stages by baffles and is completely covered with a concrete slab to provide a gas tight enclosure. The liquid and gas phases flow cocurrently through the system. The feed wastewater, recycled sludge, and oxygen gas are introduced into the first stage.

As shown in Figure 46, the oxygen gas is fed into the first stage at a slight pressure, approximately 2.5 to 10 cm (1.0 to 4.0 in) of water volume above ambient. The successive aeration states or chambers are connected to each other in such a manner as to allow gas to flow freely from stage to stage with only a slight pressure drop, but sufficient to prevent gas backmixing or interstage mixing of aeration gas. The liquid flow (mixed liquor) through successive stages is cocurrent with gas flow. Effluent mixed liquor from the system is settled in the conventional manner, and the settled activated sludge is returned to the first stage for blending with the feed raw or settled sewage.

Figure 47 depicts the general location at the treatment plant of the equipment used for flow control and mixing in the UNOX system. The UNOX box itself has a capacity of 3.1 x 10^3 m^3/day (0.8 MGD). The clariflocculator effluent and recycled sludge proceed into the inlet box and then flow through two regulatory gates into two sections of the UNOX system. The oxygen injection points are also located at the end of the box where the influent enters. The flow is then dispersed down both sides of the box through baffles and mixed by 50-hp and 40-hp motors. The effluent is then released to the clarifier and the gas is exhausted off the top (Figure 47).

The associated system for generating the oxygen needed by the UNOX system is shown in Figure 48. The pressure swing absorption (PSA) system for oxygen generation is suited to supply on-site oxygen gas for the smaller wastewater treatment plant. Main items of equipment are: 1) a feed air compressor; 2) a PSA unit skid consisting of adsorber vessels, pipe manifolded to sequencing valves; 3) a cycle control system; and 4) an instrument air dryer to provide clean dry instrument air.

The PSA system uses three adsorbent vessels to provide a continuous and constant flow of oxygen gas. The feed air is compressed by a non-lubricated compressor. As it flows through one of the adsorbent-filled adsorber vessels, the compressed air is separated into oxygen and a nitrogen-rich waste stream. The adsorbent is a granular material (molecular sieve) which attracts and traps (adsorbs) the carbon dioxide, water, and nitrogen gas, producing a relatively high purity oxygen product. While one bed is adsorbing, the other two are at various stages of regeneration.

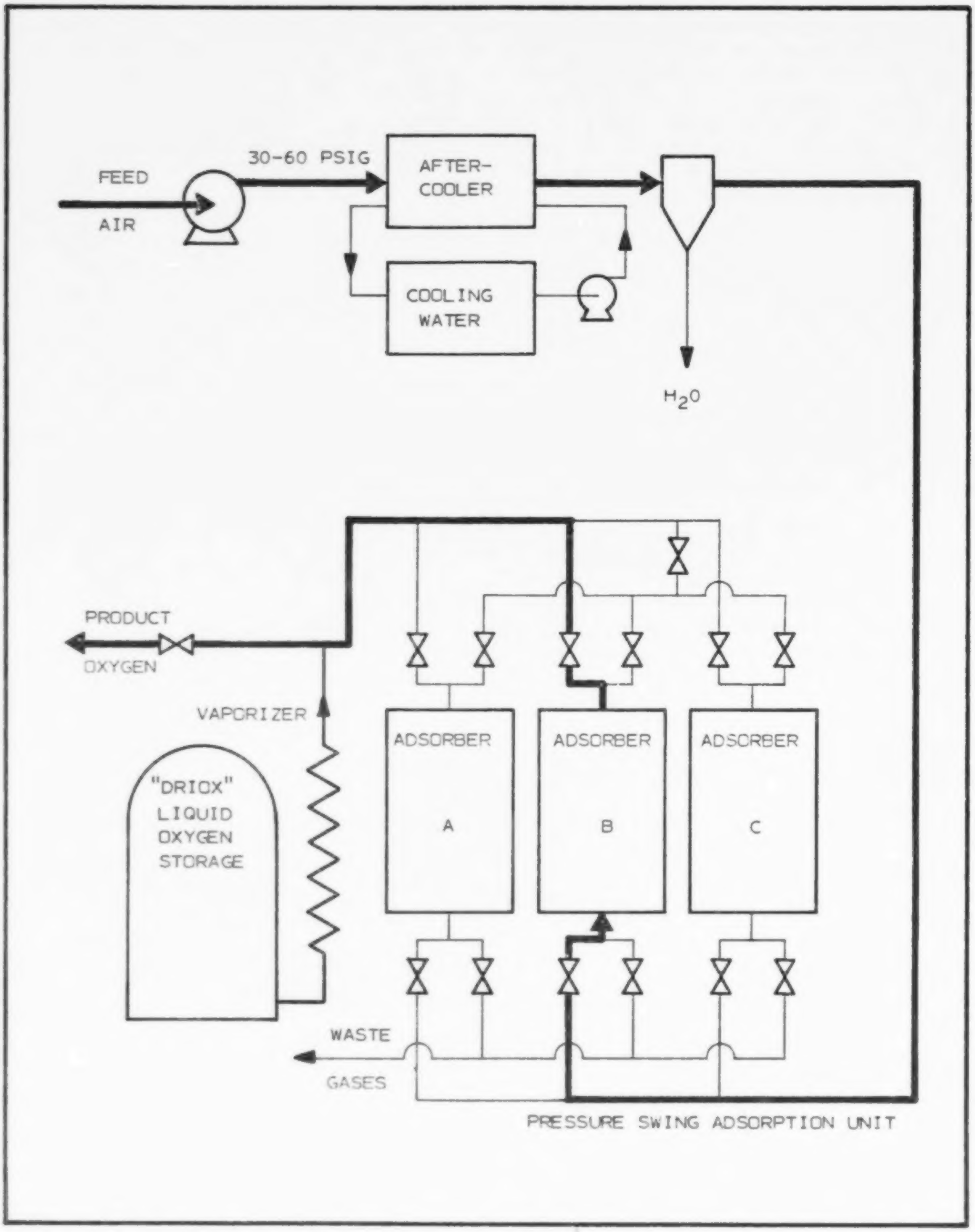

FEED
AIR
30-60 PSIG
AFTER-COOLER
COOLING WATER
H_2O
PRODUCT
OXYGEN
VAPORIZER
"DRIOX" LIQUID OXYGEN STORAGE
ADSORBER A
ADSORBER B
ADSORBER C
WASTE
GASES
PRESSURE SWING ADSORPTION UNIT

Figure 48. Flow diagram of a "lindox" PSA oxygen generating system.

The PSA oxygen generator operates on a compressor-swing, adsorption concept in which the oxygen is separated from the feed air by adsorption at high pressure, and the adsorbent is regenerated by a blow down to low pressure. The process operates on a repeated cycle: adsorption and regeneration.

During the adsorption step, feed air flows through one of the adsorber vessels until the adsorbent is partially loaded with impurities. At that time, the feed air flow is switched to another adsorber and the first adsorber is regenerated. During the regeneration step, the impurities (carbon dioxide, water, and nitrogen) are cleaned from the adsorbent so the adsorption-generation cycle can be repeated. Regeneration of the adsorber is carried out in three basic steps.

- The adsorber is depressurized to atmospheric pressure to remove some impurities from the adsorbent and to make it easy to remove the remaining impurities.

- The adsorber is purged with product oxygen to clean the remaining impurities.

- The adsorber is repressurized to adsorption pressure and is again ready to separate feed air.

A small instrument air package is also included on the PSA skid. Since the facility provides its own instrument air, the only utilities required are electric power and a small amount of city water for make-up in the closed-loop compressor after cooling system.

Only the compressor and the automatic control valves require routine maintenance. Safety is inherently incorporated into the basic process design: any hydrocarbon contaminar are also adsorbed on the bed and do not pass through the system with the oxygen product. The entire system can be started up and shut down in only a few minutes and operates completely automatically with only routine plant operator inspection.

OPERATIONAL SAFEGUARDS OF UNOX SYSTEM

1. Safeguards around the UNOX system include monitoring for explosive mixtures by strategically located hydrocarbon analyzers that cause alarms to sound and provide for automatic diversion of the UNOX influent to the shunt tanks. Severe concentrations of hydrocarbon may even shut down both the UNOX and PSA systems; such a shutdown has never occurred.

2. Foam is controlled by a series of sprays located in the influent and effluent wells of the UNOX system and in pits in the discharge line as required. Foam is piped to the shunt tanks and reprocessed. A backup antifoam system is in the planning stage.

3. The shunt tanks are also used for flow surge control by an automated system. This eliminates solids overflow from the clarifiers due to high peak flow periods.

4. Sampling throughout the wastewater treatment system is carried out using automatic samples and a timed sequence for a 24-hour period. The parameters pH, COD, BOD, TSS, and VSS are used more for monitoring than for control. Special analyses may be run on either grab or continuous samples as a given situation warrants.

OPERATIONAL PARAMETERS OF THE TREATMENT SYSTEM

The treatment plant is operated principally by monitoring the dissolved oxygen (D.O.) in the UNOX system or the partial pressure on the walls of the UNOX system. The D.O. is the principal monitoring parameter in the UNOX system; however, the partial pressure is used as a backup measurement since the D.O. probes can become fouled. The densitometers located in the clarifiers are another important monitoring aid, as they measure the density of the sludge. The densitometer, operating on a vibrating principle, senses the density of the sludges and transmits a signal that activates or deactivates a pump, thus, in part, controlling the recycle of the secondary sludge, and restricting overflow of solids from the clarifier.

There are four, 24-hour composite samples in the wastewater treatment plant at the following locations:

- Just before the flash mixer (raw effluent with solids)
- After the clariflocculator
- After the secondary clarifiers
- At the final flow measuring device.

Samples are taken at these locations and analyzed daily for pH, BOD, COD, suspended solids, and total solids. These measurements are then used as additional indications for the operation of the treatment plant.

To measure turbidity, the plant has two Hach falling stream turbidimeters on the secondary clarifier and final effluent sampling lines.

CLARIFLOCCULATOR PERFORMANCE

The plant influent passes through the flash mixer where Magnifloc 835 A (anionic) polymer is added at a rate of 1 ppm and is then discharged to the clariflocculator. During 1975, the raw waste influent flow averaged 4.31 x 10^3 m^3/day (1.1 MGD), with concentrations of 970 mg/ℓ BOD_5, 1,780 mg/ℓ COD and 1,090 mg/ℓ SS.

The clariflocculator which operates with an average hydraulic retention time of 5.25 hours provided average BOD_5, COD, and SS reductions of 26, 30 and 28 percent, respectively, which represent 29 percent of the plant BOD reduction, 38 percent of the plant COD reduction, and 37 percent of the plant SS reduction. These data are summarized in Table 87.

UNOX System Performance

During 1975, the UNOX system average influent flow was 4.3 x 10^3 m^3/day (1.1 MGD) with average concentrations of 715 mg/ℓ BOD, 1,240 mg/ℓ COD and 790 mg/ℓ SS (Table 88). The UNOX system and secondary clarifiers provided BOD_5, COD, and SS reductions of 86, 58, and 52 percent, respectively. These UNOX system reductions represented 95 percent of the plant BOD reduction, 74 percent of the plant COD reduction, and 68 percent of the plant SS reduction. Effluent from the secondary clarifiers, prior to the final "polishing" has concentrations of 90 mg/ℓ BOD and suspended solids (250 mg/ℓ may be discharged to the town plant without surcharge). As a result, final "polishing" clarification is necessary for additional solids removal. Table 89 shows overall plant performance.

Waste treated by the UNOX system has an average hydraulic retention time of 7.45 hours and a corresponding solids retention time or sludge age of 9.6 days. This system is operated with a mixed liquid suspended solids concentration of 9,250 mg/ℓ , with a 75 percent volatile fraction. The biomass loading of the influent to the UNOX system is $F_{BOD_5/M}$=0.14* and $F_{COD/M}$=0.25** The average organic loading is 10 kg BOD/m^3/day

Recycle from secondary clarifiers has an average solids concentration of 22,200 mg/ℓ (2.2 percent) at a recycle flow rate of 4.4 x 10^3 m^3/day (1.2 MGD) (102 percent of UNOX system influent flow). Sludge is wasted from the bottoms of the secondary clarifiers with an average solids concentration of 33,300 mg/ℓ (3.3 percent) at a rate of 11,200 gal per day.

Discussion of the operation and performance of the UNOX system at the chemical plant must take into account that the wastewater treatment plant as a whole was designed to pretreat

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*$F_{BOD_5/M}$=kg BOD_5/kg mixed liquor volatile suspended solids (MLVSS) per day

**$F_{COD/M}$=kg COD/kg mixed liquor volatile suspended solids (MLVSS) per day

TABLE 87. CLARIFLOCCULATOR

	Parameter	1975 Average	Range
Clarifloculator (plant) Influent Parameters	Flow	4.31×10^3 m^3/day (1.1 MGD)	$3.4\text{-}4.7 \times 10^3$ m^3/day (0.9-1.2 MGD)
	BOD$_5$	970 mg/ℓ	700-1200 mg/ℓ
	COD	1780 mg/ℓ	1000-2700 mg/ℓ
	SS	1090 mg/ℓ	620-2200 mg/ℓ
Clariflocculator Operating Parameters	BOD$_5$ reduction	26 percent	0-47 percent
	COD reduction	30 percent	3-50 percent
	SS reduction	28 percent	0-68 percent
Clariflocculator Effluent Parameters	BOD$_5$	715 mg/ℓ	380-1300 mg/ℓ
	COD	1240 mg/ℓ	560-2700 mg/ℓ
	SS	790 mg/ℓ	240-2800 mg/ℓ

TABLE 88. UNOX SYSTEM

	Parameter	1975 Average	Range
UNOX System Influent Parameters	Flow	4.3×10^3 m^3/day (1.1 MGD)	$3.4\text{-}4.7 \times 10^3$ m^3/day (0.9-1.2 MGD)
	BOD_5	715 mg/ℓ	380-1,300 mg/ℓ
	COD	1,240 mg/ℓ	560-2,700 mg/ℓ
	SS	795 mg/ℓ	240-2,800 mg/ℓ
UNOX System Operating Parameters	F_{BOD_5}/M*	.14	0.07-0.23
	F_{COD}/M**	.25	0.10-0.38
	Organic Loadings (kg BOD/m^3/day)	10	5.1-18.3
	Hydraulic Retention Time	7.45 hrs	4.0-9.2 hrs
	SRT (Sludge Age)	9.6 days	6-50 days (generally 8-24 days)
	MLSS	9,250 mg/ℓ	4,200-15,000 mg/ℓ
	MLVSS	6,875 mg/ℓ	3,500-9,800 mg/ℓ
	Recycle Flow	4.4×10^3 m^3/day	$3.7\text{-}5.5 \times 10^3$ m^3/day
	Recycle SS	22,200 mg/ℓ (2.2 percent)	14,000-40,000 mg/ℓ
	Waste Sludge-Flow	42.4 m^3/day (11,200 gal/day)	5.3-113.6 m^3/day (1,400-30,000 gal/day)
	Waste Sludge-Solids	33,300 mg/ℓ (3.3 percent)	26,000-50,000 mg/ℓ
	BOD_5 Reduction	86 percent	81-91 percent

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*$\frac{F_{BOD_5}}{M}$ = kg BOD_5 influent per day per kg mixed liquor volatile suspended solids (MLVSS) in UNOX system

**$\frac{F_{COD}}{M}$ = kg COD influent per day per kg mixed liquor volatile suspended solids (MLVSS) in UNOX system

TABLE 88 (continued)

	Parameter	1975 Average	Range
	COD Reduction	58 percent	24-81 percent
	SS Reduction	52 percent	17-87 percent
UNOX System (secondary clarifier) Effluent Parameters	BOD_5	100 mg/ℓ	200-220 mg/ℓ
	COD	550 mg/ℓ	200-15,000 mg/ℓ
	SS	380 mg/ℓ	60-16,000 mg/ℓ

TABLE 89. PLANT SUMMARY

	Parameter	1975 Average	Range
Plant Influent	Flow	4.3×10^3 m^3/day (1.1 MGD)	3.4-4.7
	BOD_5	970 mg/ℓ	700-1,200 mg/ℓ
	COD	1,780 mg/ℓ	1,000-2,700 mg/ℓ
	SS	1,090 mg/ℓ	380-1,300 mg/ℓ
Plant Operating	BOD_5 Reduction	91 percent	86-95 percent
	COD Reduction	78 percent	67-86 percent
	SS Reduction	76 percent	32-94 percent
Plant Effluent	BOD_5	90 mg/ℓ	50-210 mg/ℓ
	COD	390 mg/ℓ	180-1,200 mg/ℓ
	SS	260 mg/ℓ	50-500 mg/ℓ

variable, high strength industrial wastewater prior to discharge to a municipal wastewater treatment system. As a result, the UNOX system is operated with a relatively high mixed liquor SS concentration and relatively low F/M ratios in order to accommodate the variable nature of the influent wastewater. Similarly, the recycle flow from the secondary clarifiers to the head of the UNOX tank is generally equal to or greater than 100 percent of the flow of wastewater influent to the UNOX system. This high percent recycle helps to maintain the large concentrations of MLSS desired, increase the solids retention time (sludge age), and reduce the opportunity for the highly oxygen demanding wastes sent to the secondary clarifiers of becoming anaerobic prior to being recycled.

The UNOX system efficiencies were analyzed by plotting BOD and COD percent removals and effluent concentrations vs. the respective F/M ratios as well as solids retention times (sludge ages) as seen in Figures 49 through 52. The data for each respective graph is given in Tables 90 through 93. Generally, the highest percent removals of BOD from the wastewaters influent to the UNOX system occurred as sludge ages increased and F/M ratios decreased. Effluent quality in terms of concentrations of BOD, COD, and SS discharged from the secondary clarifiers improved (concentrations discharged decreased) as solids retention times increased and F/M ratios decreased. No relationships appear to exist for the percent removal of suspended solids by the UNOX system.

It is impossible to identify the optimum F/M ratios for maximum BOD and COD percent removals, because of variations in data. However, it is apparent that the percent removal of COD deteriorates significantly at F_{COD}/M ratios greater than 0.3 or sludge ages of less than 10 days. Similarly, there appears to be a slight reduction in the percent removal of BOD at F_{BOD_5}/M ratios greater than 0.2 and again with sludge ages of less than 10 days.

These F/M ratios, at which removal efficiencies and effluent quality begin to deteriorate, are somewhat lower than anticipated. In general, UNOX systems for industrial wastes are designed to operate at F_{BOD}/M ratios of between 0.2 and 0.8. In terms of sludge ages, deterioration of percent removals and effluent qualities at sludge ages of less than 10 days seem somewhat low since most industrial pure oxygen systems operate with sludge ages between 8 and 20 days.

ECONOMIC EVALUATION

Construction and operation and maintenance cost information for a hypothetical UNOX system for processing industrial-chemical wastewater was provided by Union Carbide Corp. Design assumptions used in the development of this cost information are shown

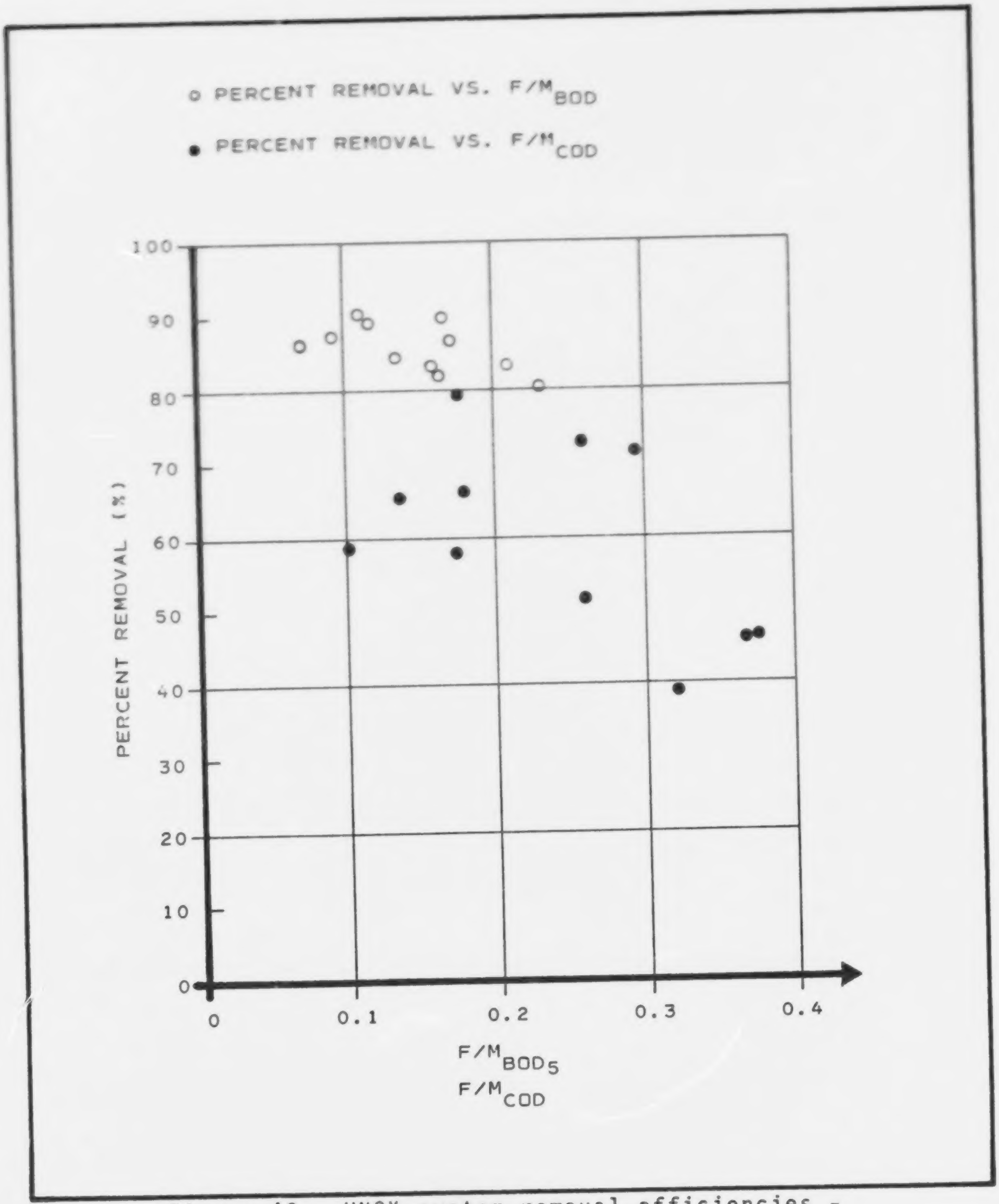

Figure 49. UNOX system removal efficiencies - (MLVSS used in F/M calculations).

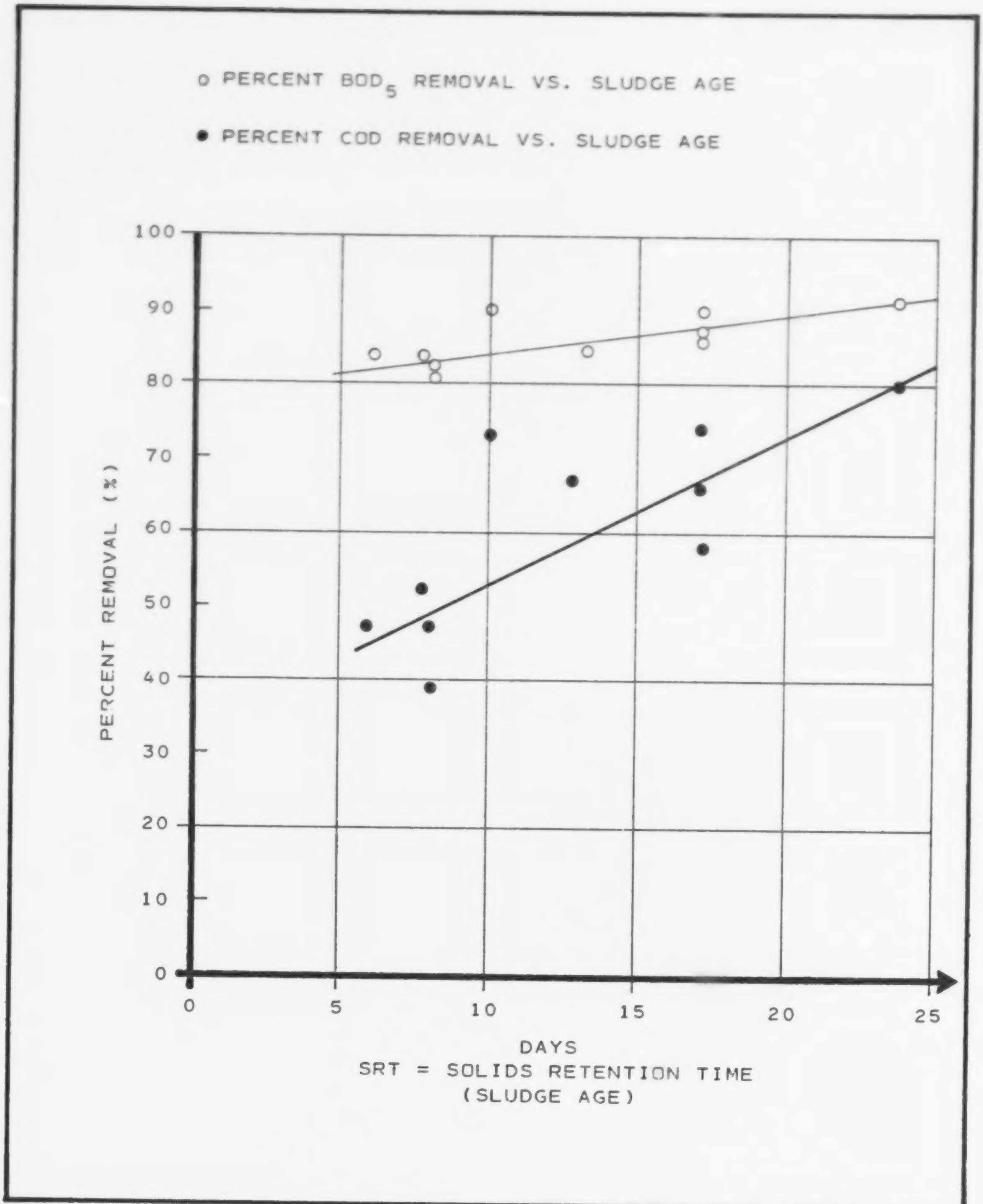

Figure 50. UNOX system removal efficiencies - BOD_5 and COD vs. sludge age.

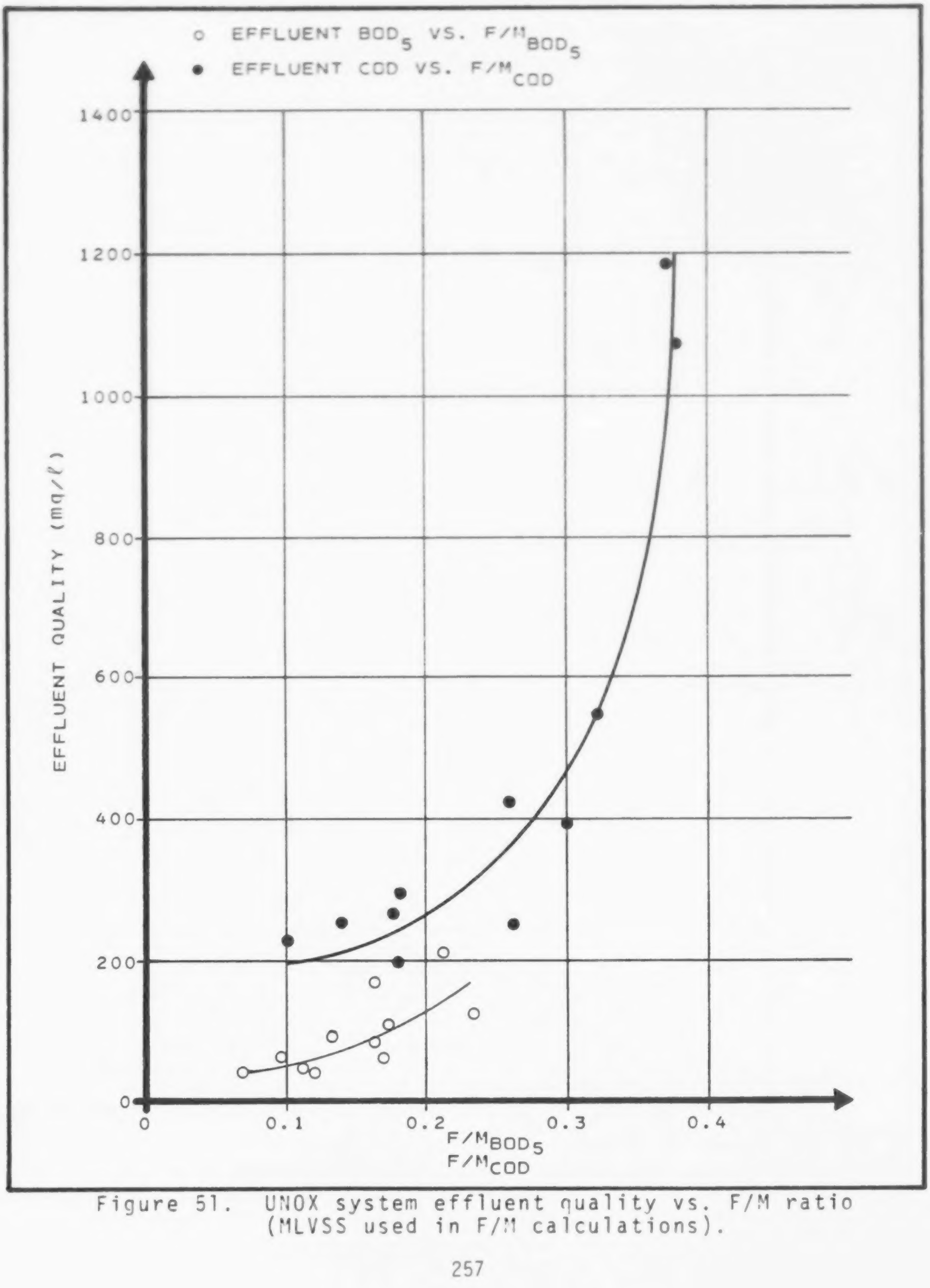

Figure 51. UNOX system effluent quality vs. F/M ratio (MLVSS used in F/M calculations).

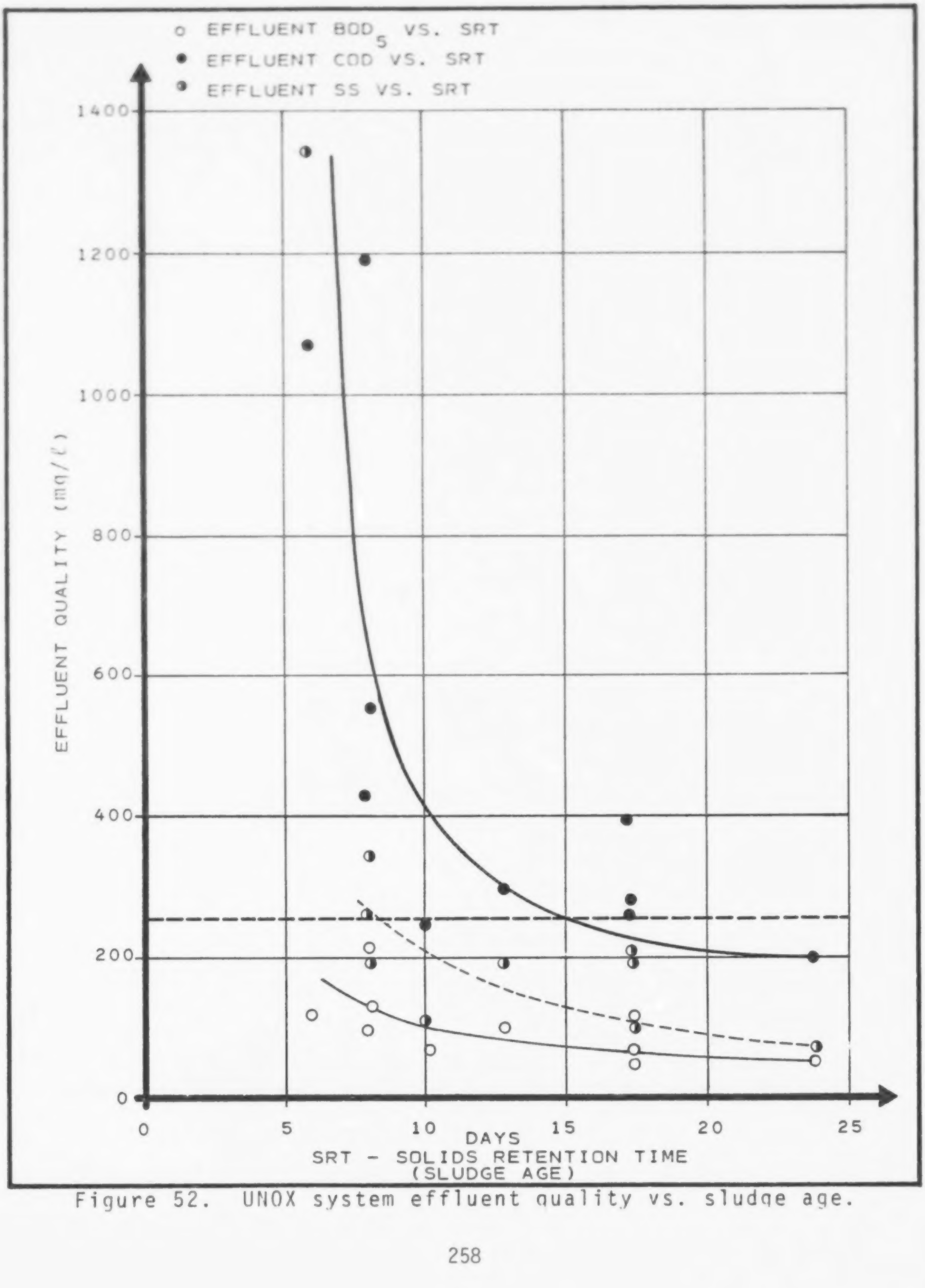

Figure 52. UNOX system effluent quality vs. sludge age.

TABLE 90. DATA ON F/M RATIOS AND CORRESPONDING PERCENT REMOVALS AS PLOTTED IN FIGURE 49

F_{BOD_5}/M	% BOD_5 Removal
.069	87
.094	88
.111	91
.117	90
.132	85
.160	84
.161	83
.168	90
.171	87
.210	83
.233	81
F_{COD}/M	% COD Removal
.102	59
.138	66
.175	58
.177	80
.180	67
.258	52
.260	73
.297	72
.322	39
.371	47
.379	47

TABLE 91. DATA ON SLUDGE AGE AND CORRESPONDING PERCENT REMOVALS AS PLOTTED IN FIGURE 50

Solids Retention Time (Sludge Age)	% BOD_5 Removal	% COD Removal
5.9	83	47
7.8	84	52
8.0	83	47
8.1	81	39
10.0	90	73
12.7	85	67
17.3	90	58
17.3	88	66
17.3	87	72
23.9	91	80
49.7	87	59

TABLE 92. DATA ON F/M RATIOS AND CORRESPONDING EFFLUENT QUALITIES AS PLOTTED IN FIGURE 51

F_{BOD_5}/M	Effluent BOD_5 (mg/ℓ)
.069	47
.094	62
.111	57
.117	42
.132	99
.160	91
.161	158
.168	62
.171	111
.201	212
.233	124

F_{COD}/M	Effluent COD (mg/ℓ)
.102	229
.138	257
.175	286
.177	200
.180	296
.258	425
.260	249
.297	397
.322	550
.371	1189
.379	1077

TABLE 93. DATA ON SLUDGE AGE AND CORRESPONDING EFFLUENT QUALITIES AS PLOTTED IN FIGURE 52

Solids Retention Time (Sludge Age)	Effluent BOD_5 (mg/ℓ)	Effluent COD (mg/ℓ)
5.9	158	1077
7.8	91	425
8.0	212	1189
8.1	124	550
10.0	62	249
12.7	99	296
17.3	42	286
17.3	62	257
17.3	111	397
23.9	57	200
49.7	47	229

in Table 94. Additional estimates for sludge disposal costs and miscellaneous supplies were derived from Hovious et al. (59) and updated to 1976 costs.

Table 95 shows the estimated 1976 construction costs for the system. The total cost, including contractor and engineering design services and construction contingencies is \$2,113,000 for a 5.68×10^3 m^3/day (1.5 MGD) plant, amortized over 20 years at six (6) percent to yield a total investment of \$184,000. This investment and estimated operation and maintenance costs are shown in Table 96. Operating labor is based on one operator per shift. Power requirements include electric motor drive for mixing in the UNOX tank and operation of the oxygen generation plant.

The specified flow and influent and effluent BOD concentration data shown in Table 89 were used to determine the quantity of BOD removed per year. This information was used in association with the total operation and maintenance cost of \$437,800/year to derive a cost of \$0.15/kg (\$0.15/lb) BOD removed for the UNOX system. The total treatment costs for the facility have been estimated at \$0.55/kg BOD removed. This figure represents costs for primary treatment, the UNOX system, allowance for downtime, and for further disposal of effluents or sludge.

TABLE 94. DESIGN ASSUMPTIONS UTILIZED IN DEVELOPMENT OF UNOX SYSTEM COSTS

Flow: 5.68×10^3 m^3/day (1.5 MGD)

influent BOD: 1,500 mg/ℓ

influent suspended solids: 1,000 mg/ℓ

COD/BOD ratio: 1.5

retention time: 18.4 hrs

F/M ratio: 0.4

MLVSS: 4,900 mg/ℓ

recycled solids: 2.9%

overflow rate: 18.3 m^3/day/m^2

oxygen supply: 11.8 t (13.0 tons)

oxygen utilization: 82%

dissolved oxygen: 5.0 mg/ℓ

effluent BOD: 120 mg/ℓ

TABLE 95. UNOX FACILITY: ESTIMATED CONSTRUCTION COSTS - 1976*

Equipment	$ 883,000
Labor	314,000
Materials	320,000
	$1,517,000
Contractor overhead and profit	142,000
Engineering design services	249,000
Total Installed Cost	$1,908,000
Contingency	205,000
TOTAL	$2,113,000

*Includes secondary clarifier, a three-stage UNOX tank (50.2 m x 16.7 m; 5.2 m sidewater depth and 0.75 m freeboard, and oxygen generation equipment. Does not include primary clarifier, sludge handling equipment, buildings, or off-site electrical service.

TABLE 96. UNOX SYSTEM: ESTIMATED O&M COSTS - 1976*

Operating Labor	$ 20,000
Power (HP x 77.78)**	
Mixing	13,500
O_2 generation	20,000
Maintenance (2 percent of construction)	42,300
Misc. Supplies***	1,000
Sludge Disposal*** (BOD_r x \$ 0.034/kg BOD_r x 10% annual inflation since 1971)	157,000
Amortize Investment**** (20 yrs at 6 percent)	184,000
TOTAL	$437,800

*This estimate is for the UNOX System only, and does not include costs for primary treatment, allowance for downtime, or costs for effluent or sludge disposal.

**From aeration and power cost data at 40-Acre facility.

***From 1971 data presented in reference

****Capital recovery factor = 0.08718. Salvage value not included.

SECTION V

SAMPLING ACTIVITIES

INTRODUCTION

During the initial phase of this study, four sites were visited to evaluate design and operational data at facilities successfully treating organic industrial wastes. The four sites were:

- Washburn Tunnel Facility, Pasadena, Texas:

  This 1.7×10^5 m^3/day (45 MGD) completely mixed activated sludge facility treats wastes from a kraft paper mill (70 percent) and four petrochemical plants with BOD and COD loadings of 57,173 and 202,344 kg/day (126,045 and 446,169 lb/day), respectively. BOD_5 and COD removal efficiencies were 91 and 70 percent. Phenols and oil and grease were also significantly reduced during the 17-hr period in the system.

- 40-Acre Facility, Texas City, Texas:

  The 40-Acre Facility, a lagoon system on the Gulf Coast, employs anaerobic-microaerobic-aerobic-facultative treatment to process a mixed petrochemical waste flow of approximately 5.3×10^4 m^3/day (14.0 MGD). The plant actually covers 64 ha (160 ac). Lagoon volume ameliorates shock loading effects. The system, which has been highly successful in reducing marginally degradable organic material, has a possible 22-day retention time. It treats BOD_5 loading of 26,100 kg/day (57,550 lb/day) and COD loading of 50,438 kg/day (111,197 lb/day) with BOD_5 and COD removal efficiencies of 96 and 76 percent, respectively.

- Deep Shaft Facility, Paris, Ontario:

  Costs of the Deep Shaft system are low in terms of oxygen transfer and site area requirements. The Paris facility treats a waste stream from a variety of industries; average flow is 4.73×10^2 m^3/day (0.13 MGD), with BOD_5 loading of 78 kg/day (172 lb/day)and COD loading of 253 kg/day (558 lb/day),with BOD_5 and COD removal efficiencies of 82 and 82 percent, respectively.

- UNOX Pure Oxygen System:

  The UNOX system treats wastes from a chemical manufacturing plant; flow averages 4.3 x 10^3 m^3/day (1.14 MGD), BOD_5 loading of 3,075 kg/day (6,780 lb/day) and COD loading of 5,332 kg/day (11,760 lb/day), with reported BOD_5 and COD removal efficiencies of 95 and 74 percent, respectively.

The case studies included acquisition of all available data for the following areas:

- Influent effluent waste stream constituents and overall treatment efficiency
- Overall plant design and operational details
- Design and operational details for specific plant components used for enhancing biodegradation
- Organic wastes not amenable to biodegradation
- Impact of treatment plant effluents on environment
- Unique or specially acclimated in-plant biota capable of degrading refractory organic materials
- Cost and energy demands for plant construction, operation, and maintenance.

As expected, different quantities and types of information were available at each of the four plants. Both qualitative and quantitative determinations of hazardous organic wastes in the waste streams were generally lacking. Gross measurements of organic materials such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total organic carbon (TOC) are of limited value in evaluating biological treatment of specific hazardous organic materials.

The efficiency of biodegradation of specific problematic organic wastes must be measured in terms of complete oxidation or biochemical alteration of the substrate into substances no longer considered either environmentally hazardous or toxicological. Removal of such wastes in an unaltered state through adsorption into settleable biological flocs may result in significant removal from the aqueous waste stream, yet the sludges produced by the treatment process may exhibit the hazardous properties of the removed constituents and cause sludge disposal problems.

Since the sludge particles of secondary biological waste treatment systems are essentially organic, they can provide substrate for adsorption of colloidal or dissolved organic hazardous wastes. It is suspected that this phenomenon may be important when comparing various treatment alternatives.

The two major goals of the second phase of this project were to determine:

- The efficiencies of different biological treatment systems in removing hazardous organic materials from waste streams
- The mode of removal of hazardous organic materials by different biological systems, either via biodegradation or in association with secondary sludges.

In addition to these goals, Phase Two was designed to:

- Identify and characterize the microbial populations in the biological systems studies
- Determine the environmental sink of specific organic materials discharged with the plant effluent.

Section V presents the specific sampling activities and the sampling results for the individual case study sites. Appendix B presents the rationale for the selection of the organic and biological parameters measured and the sampling stations and frequency, as well as the sampling and analytical methods.

Due to proprietary considerations, sampling was not possible at the UNOX pure oxygen treatment plant.

SPECIFIC SAMPLING ACTIVITIES AND RESULTS

40-Acre Facility

The 40-Acre Facility in Texas City, Texas is a lagoon system treating predominately petrochemical wastewater. The 64-ha (160-ac) facility includes pH adjustment (HCl), nutrient addition (H_3PO_4,NH_3), equalization, two anaerobic lagoons, one limited aeration lagoon, two aeration basins, and two quiescent facultative lagoons, Flow ranges from 49 to 57 x 10^3 m^3/day (12.9 to 15.1 gal/day).

Samples were taken at 40-Acre for four days, December 15 to 18, 1977. During the sampling period, the wastewater treatment scheme consisted of equalization, limited aeration, parallel flow through the aerated stabilization basins, settling in facultative lagoon #1 and discharge to the Hurricane Levee Canal. A characterization of the facility influent-effluent loading values for conventional parameters for the sampling period is shown in Table 97.

Sampling Sites and Frequency--

Figure 53 shows the sites selected for sampling at the 40-Acre Facility, and Table 98 lists both organic and biological samples taken, their location, and sample identification designation. The following discussion explains the selection of the sampling sites.

Four waste streams are treated at 40-Acre. Influents A, B, and C enter the system at influent point 1 and influent D at influent point 2 (Figure 53). Influents A and C (40-A-ORG-COMP-1I) were composite-sampled at a confluent wet well at influent point 1. Piping for influent B did not allow composite sampling of influent B and the other waste streams entering at influent point 1. Fortunately, a draw-off spigot had been installed in the influent B pipe. Daily grab samples from this spigot were proportioned using daily flow data and mixed with the 40A-ORG-COMP-1I composite sample. Influent D (40A-ORG-COMP-2I) was composite-sampled at the influent wet well to the aeration basins.

Samples were taken from the limited aeration basin effluent (40A-ORG-COMP-3E) and settled sludge (40A-ORG-COMP-6), and the waste flows from both aeration basins (40A-ORG-COMP-4E). A single grab sample was taken for the organic analysis of the sludge from the facultative lagoons (40A-ORG-COMP-7). A portion of the GCWDA daily effluent composite sample was used for organic analysis (40A-ORG-COMP-5E).

Sediment samples for organic analyses were grabbed from the Hurricane Levee Discharge Canal with the La Motte Dredge: one at the 40-Acre effluent outfall (40A-ORG-COMP-2B) and one upstream of the outfall (40A-ORG-COMP-1B). Approximate sampling locations are shown in Figure 53.

Biological samples for the microbial population study were grabbed from various lagoons. All the lagoons active in the treatment chain were sampled, as well as two inactive lagoons, one facultative, the other anaerobic. Facultative lagoon #2 (40A-BIO-GRAB-5S) and anaerobic lagoon #2 (40A-BIO-GRAB-1S) had been inactive for 3 and 8 mo, respectively.

Chemical Analyses Results--

The results for the organic analyses of the samples taken at the 40-Acre Facility are presented in Tables 99 through 101. The sample designations used in these tables are based on station location and are explained in Table 98 and shown in Figure 53.

Table 99 shows the organic chemical constituents present in the two influent sources to 40-Acre (40A-ORG-COMP-1I and 2I);

TABLE 97. CHARACTERIZATION OF 40-ACRE WASTEWATER AND EFFLUENT LOADING IN KG/DAY (LB/DAY) FOR THE SAMPLING PERIOD

Wastewater Characteristic	Wastewater Loading	Effluent Loading	Percent Removal
Flow x 10^4 m^3/day (MGD)	5.3 (13.9)	5.0 (13.2)	
TOC	15,396 (33,871)	2,979 (6,567)	81
COD	46,241 (101,730)	9,283 (20,466)	80
BOD	22,922 (50,428)	1,850 (4,070)	92
TSS	14,134 (36,095)	1,830 (4,026)	87
VSS	3,829 (8,424)	1,395 (3,069)	64
NH_3-N	339 (746)	256 (563)	25
Phenol	25.2 (55.4)	1.13(2.49)	96

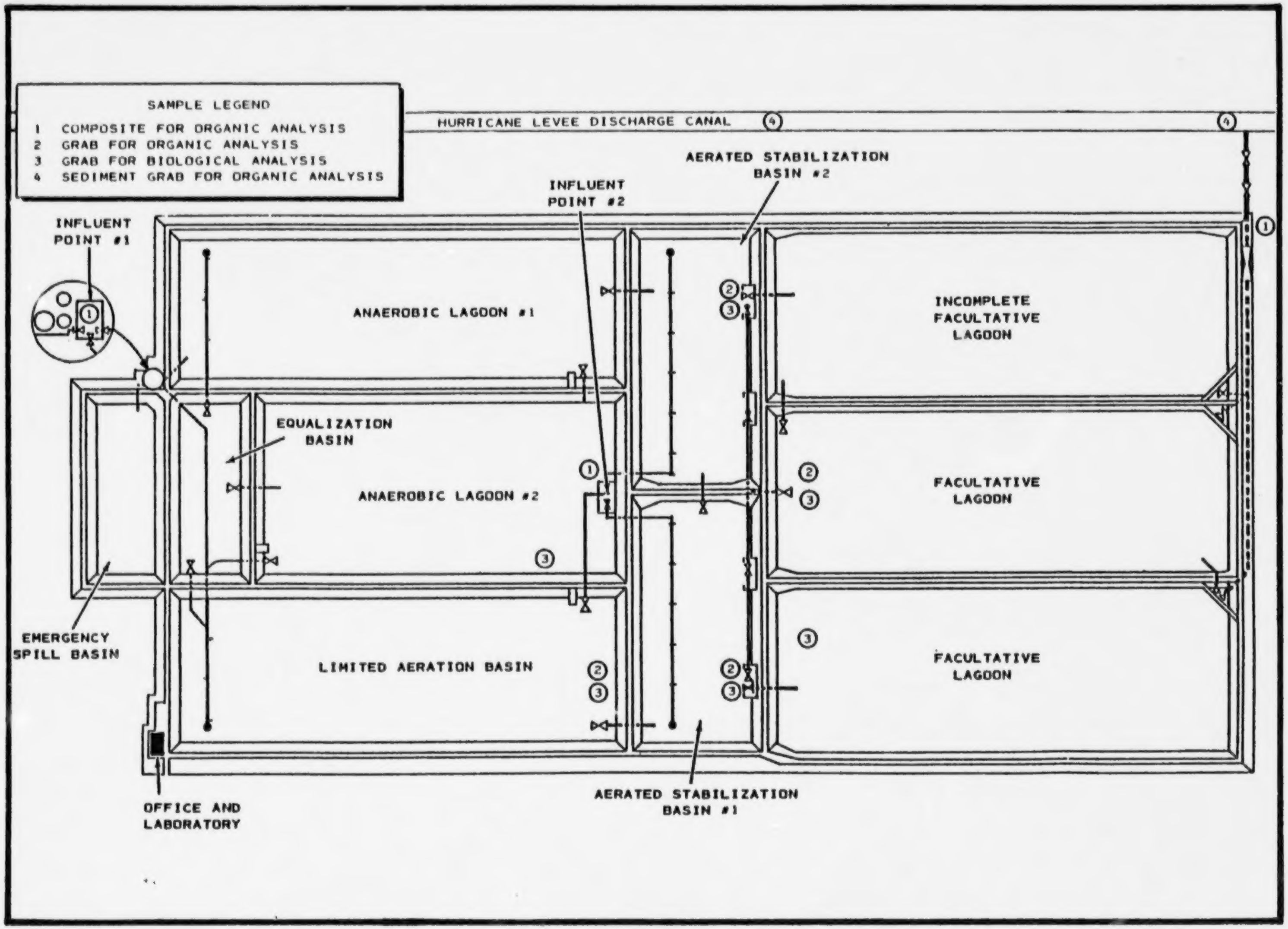
SAMPLE LEGEND
1 COMPOSITE FOR ORGANIC ANALYSIS
2 GRAB FOR ORGANIC ANALYSIS
3 GRAB FOR BIOLOGICAL ANALYSIS
4 SEDIMENT GRAB FOR ORGANIC ANALYSIS
HURRICANE LEVEE DISCHARGE CANAL
AERATED STABILIZATION BASIN #2
INFLUENT POINT #2
INFLUENT POINT #1
ANAEROBIC LAGOON #1
EQUALIZATION BASIN
ANAEROBIC LAGOON #2
LIMITED AERATION BASIN
EMERGENCY SPILL BASIN
OFFICE AND LABORATORY
AERATED STABILIZATION BASIN #1
INCOMPLETE FACULTATIVE LAGOON
FACULTATIVE LAGOON
FACULTATIVE LAGOON
①
②
③
④

Figure 53. GCWDA 40-Acre Facility layout and sampling sites.

TABLE 98. 40-ACRE FACILITY ORGANIC AND BIOLOGICAL SAMPLES LOCATIONS AND IDENTIFICATION DESIGNATIONS

A. Samples for Organic Analysis

LOCATION	DESIGNATION
Influent to equalization basin	40A-ORG*-COMP*-1I
Influent to aeration basins	40A-ORG-COMP-2I
Effluent from limited aeration basin	40A-ORG-COMP-3E
Effluent from aeration basins	40A-ORG-COMP-4E
Effluent from facultative lagoon	40A-ORG-COMP-5E
Sludge from limited aeration basin	40A-ORG-COMP-6
Sludge from facultative lagoon	40A-ORG-COMP-7
Sediment upstream of outfall	40A-ORG-COMP-1B
Sediment at outfall	40A-ORG-COMP-2B

B. Samples for Biological Analysis

LOCATION	DESIGNATION
Anaerobic lagoon #2	40A-BIO*-GRAB*-1S
Limited aeration basin	40A-BIO-GRAB-2S
Aeration basins #1 & #2	40A-BIO-GRAB-3S
Active facultative lagoon	40A-BIO-GRAB-4S
Inactive facultative lagoon	40A-BIO-GRAB-5S

*Notes.
ORG - organic analysis samples.
COMP - composite samples taken according to Sampling Methods.
BIO - biological samples for microbial analysis.
GRAB - grab samples taken according to Sampling Methods.

TABLE 99. RESULTS OF GC ANALYSIS OF COMBINED EXTRACTS OF BASE/NEUTRAL AND ACID FRACTIONS ISOLATED FOR 40-ACRE SAMPLES (concentration values in µg/l, with no entry representing concentrations below detection limits)

Constituent	Samples (40A-ORG-COMP-)					
	1I	2I	3E	4E	5E	6
Halogenated Aliphatics						
Bis (2-chloroethoxy) methane	8.0	25.0	-	1.0	-	-
Ethers						
Bis (2-chloroisopropyl) ether	16.0	2.0	-	-	-	-
Chloroethyl ether	1.0	-	-	-	-	-
4-Bromophenyl ether	7.0	-	-	-	-	-
Monocyclic Aromatics						
Nitrobenzene	58.0	3.0	14.0	-	-	-
2, 6-Dinitrotolvene	0.2	2.0	-	3.0	-	0.2
2, 4-Dinitrotolvene	8.0	12.0	2.0	-	0.4	0.2
Hexachlorobenzene	-	4.0	-	-	-	-
1, 2-Dichlorobenzene	0.3	-	-	-	-	-
Phenols and Cresols						
Phenol	2.0	1.0	-	-	-	0.4
4-Nitrophenol	-	-	-	-	1.0	-
Pentachlorophenol	-	-	-	-	4.0	-
p-chloro-m-cresol	7.0	-	-	-	-	-
2-Chlorophenol	0.6	-	-	-	-	-
Phthalate Esters						
Dimethyl phthalate	6.0	8.0	-	6.0	0.2	1.0
Diethyl phthalate	4.0	2.0	40.0	4.0	-	2.0
Dibutyl phthalate	13.0	1.0	-	1.0	-	1.0
Butyl benzyl phthalate	-	6.0	-	6.0	1.0	2.0
Bis (2-ethylhexyl) phthalate	-	60.0	21.0	1.0	-	1.0
Polycyclic Aromatic Hydrocarbons						
Naphthalene	0.5	1.0	-	-	-	-
Acenaphthylene	3.0	2.0	-	5.0	1.0	0.2
Acenaphthene	13.0	4.0	19.0	4.0	0.4	0.2
Fluorene	0.6	16.0	6.0	0.2	12.0	1.0
Phenanthrene	4.0	1.0	26.0	3.0	1.0	-
Fluoranthene	1.0	2.0	47.0	-	4.0	3.0
Pyrene	0.6	3.0	-	1.0	-	-
Benzo(b) fluoranthene	-	12.0	-	0.4	-	-
Benzo(a) pyrene	-	3.0	-	2.0	-	-
Benzo(a) anthracene	-	-	-	1.0	2.0	0.4

TABLE 99 (continued)

Constituent	Samples (40A-ORG-COMP-) 1I	2I	3E	4E	5E	6
Pesticide						
Isophorone	15.0	3.0	1.0	2.0	1.0	1.0
PCB's and Related Compounds						
2-Chloronaphthalene	0.9	19.0	18.0	-	-	0.4
Nitrosamines and Other N-Compounds						
1, 2-Diphenylhydrazine	73.0	5.0	27.0	14.0	0.4	0.4
Nitrosodiphenylamine	-	3.0	-	1.0	0.2	-
Benzidene	1.0	12.0	32.0	7.0	8.0	5.0

TABLE 100. RESULTS OF GC/MS ANALYSIS OF 40-ACRE SLUDGE SAMPLE: 40A-ORG-COMP-7

(concentration values in μg/l)

Constituent	Concentration
Halogenated Aliphatics	
Bis (2-chloroethoxy) methane	4.0
Dichloromethane	12.0
1, 1-Dichloroethene	3.0
1-Dichloroethene	0.5
Trichloromethane (chloroform)	32.0
1, 1, 2, 2-Tetrachloroethane	0.9
Trichloroethene	0.6
Ethers	
Bis (2-chloroisopropyl) ether	11.0
Monocyclic Aromatics	
Nitrobenzene	3.0
2, 4-Dinitrotoluene	20.0
2, 6-Dinitrotoluene	1.0
Benzene	35.0
Toluene	5.0
Phenol and Cresols	
Phenol	10.0
2, 4-Dimethylphenol	1.0
4-Nitrophenol	14.0
Phthalate Esters	
Dimethyl phthalate	3.0
Dibutyl phthalate	1.0
Butyl benzylphthalate	5.0
Dioctylphthalate	15.0
Polycyclic Aromatic Hydrocarbons	
Naphthalene	4.0
Acenaphthylene	70.0
Acenaphthene	2.0
Fluorene	20.0
Phenanthrene	4.0
Fluoranthene	11.0
Pyrene	3.0
Benzo(a) pyrene	6.0

TABLE 100 (continued)

Constituent	Concentration
Nitrosamines and Other N-Compounds	
1, 2-Diphenylhydrazine	8.0
Benzidine	3.0
PCB's and Related Compounds	
2-Chloronaphthalene	15.0
Pesticides	
Isophonone	2.0

TABLE 101. RESULTS OF GC AND GC/MS ANALYSES OF 40-ACRE SEDIMENT SAMPLES

(concentration values in μg/kg dry weight, with no entry representing concentrations below detected limits)

Constituent	Sample (40A-ORG-COMP-) 1B	2B
Halogenated Aliphatics		
Dichloromethane (methylene chloride)	47.0	35.0
Trichloromethane (chloroform)	61.0	50.0
Trichloroethene	-	0.8
1, 1, 2-Trichloroethane	2.0	-
1, 3-Dichloropropene	2.0	-
Monocyclic Aromatics		
Benzene	28.0	20.0
Toluene	4.0	5.0
Phthalate Esters		
Dimethyl phthalate	43.0	46.0
Bis (2-ethylhexyl) phthalate	99.0	60.0
Polycyclic Aromatic Hydrocarbons		
Benzo(a)pyrene	26.0	14.0
Acenaphthylene	22.0	50.0
Fluorene	-	60.0
Fluoranthene	99.0	55.0
Pyrene	-	14.0
Nitrosamines and other N-Compounds		
1, 2-Diphenylhydrazine	22.0	46.0
Benzidine	250.0	69.0
Pesticides		
Isophorone	13.0	32.0

the effluent from the limited aeration, aeration, and facultative lagoons (40A-ORG-COMP-3E, 4E, and 5E); and the sludge from the limited aeration basin (40A-ORG-COMP-6). Tables 100 and 101 show the levels of similar organics detected in the settled biological sludge from the facultative lagoon (40A-ORG-COMP-7) and the sediment of the Hurricane Levee Discharge Canal (40A-ORG-COMP-1B and 2B), respectively.

Discussion of Results--

Comparison of the concentrations of organic constituents in the 40-Acre lagoon system influent-effluent (Table 99) shows good assimilation of many groups of wastes, but the concentrations of some constituents show atypical action. Pentachlorophenol, 4-nitrophenol, and phenolic compounds are evident in the effluent, but are not identifiable in the system influent. Chemical or biochemically induced changes in substrates can occur within the system, resulting in relatively large differences between materials in the effluent and that originally introduced.

Based on influent-effluent comparisons, all classes of wastes show a removal efficiency of 90 percent or greater for the majority of the member compounds.

Nitrobenzene, a monocyclic aromatic, was reduced from an influent concentration of 58.0 µg/ℓ to below detection limits (0.1 µg/ℓ). Previous work reported by Pitter has shown a 98-percent reduction of the influent concentration when nitrobenzene was used as the sole carbon source by an acclimated activated sludge (122). Phthalate esters have been reported to be 98 percent removed after 5 days incubation in a freshwater hydrosoil (78). The results reported here concur with these observations. Removal of phthalate esters by the lagoon system was significant. Fluorene was the only polycyclic aromatic hydrocarbon not substantially reduced in the system. Removal was 25 percent, a reduction more attributable to dilution of the influent concentration than to removal. In addition, other organic compounds removed by the lagoon system included:

- Isophorone, a pesticide (93 percent removal)
- 1,2-Diphenylhydrazine, a nitrosamine (99 percent removed)
- 2-Chloronaphthalene, a PCB-related compound (removed from 19 µg/ℓ to below detection limits).

Biological treatment performance is difficult to evaluate without information on both percent oxidation and percent removal by physicochemical processes but not degraded. A determination of the organic materials adsorbed intact into the sludge material (Table 100) gives an indication of the oxidative capability of the biological system. The number and quantities of organic compounds identified in the sludge are an indication of the importance of a biological sludge as a sink for recalcitrant organics. For example, many more halogenated aliphatics were identified in the sludge than in the wastewater (Table 99). There are two explanations for this phenomenon: the halogenated aliphatics may be intermediate products from the oxidation of other organics, or the organics were adsorbed prior to the sampling period and are relatively non-degradable in biological systems.

Fluorene was the only compound that did not show a substantial reduction in the influent-effluent comparisons. The fluorene sludge value was 20.0 μg/ℓ, greater than either the influent or effluent values. This may indicate that the adsorption capacity of the biological sludge for fluorene has been exceeded and that it is not treatable in the concentration detected.

Five compounds (napthalene, acenaphthylene, 2,4-dinitrotoluene, phenol, and 4-nitrophenol) were observed to have higher concentrations in the biological sludge than in the wastewater. Acenaphthylene, for example, has a much higher sludge concentration (70.9 μg/ℓ) than wastewater concentration (1.0 to 5.0 μg/ℓ). This suggests these are biochemically recalcitrant or inert compounds. In addition, the pesticide, 2-chloronaphthalene, has a sludge concentration (15.0 μg/ℓ) close to the influent concentration (19.0 μg/ℓ).

Conversely, low concentrations of other organic constituents in the sludge and effluent indicate oxidation of these materials. Organics in this category are: bis- (2-chloroethoxy) methane, nitrobenzene, dibutyl phthalate, acenaphthene, phenanthrene, 1,2 diphenylhydrazine, and benzidine.

Table 101 presents the results of the analyses of the sediments from the Hurricane Levee Discharge Canal; 40A-ORG-COMP-1B was taken 90 m (300 ft) from the 40-Acre effluent point, and 40A-ORG-COMP-2B was taken at the effluent point. These data indicate that the sediment of the receiving waters is a sink for organic materials. Higher organic concentrations were found in the sediment samples than in the biological sludge sample. No ethers or phenol and cresol compounds were identified in the sediments.

Two mechanisms are responsible for the partitioning of organics into the sediment: the affinity of clay particles (the predominate soil constituent found in the sediments) for organic molecules, or the salting out of organic molecules in the brackish water of the Hurricane Levee Discharge Canal.

Biological Analyses Results--

Wet mount, gram-stain, and identification summary--The anaerobic lagoon (40A-BIO-GRAB-1S) contained gram-negative, feebly motile rods, mostly in pairs (Pseudomonas sp); many gram-negative, curved (vibroid) forms (Comamonas sp); and many large, gram-positive yeast cells with budding. In addition, an unusual unidentified bacteria, gram-negative and nonmotile, was found in the anaerobic lagoon. This bacteria was curved to such an extent that the ends of the microbe almost met. A photosynthetic bacteria belonging to the family Thiohodaceae was also identified in the anaerobic lagoon.

The flora found in the aeration basins and active facultative lagoon contained predominately gram-negative microbes. These included Pseudomonas, Caulobacter, Arthrobacter, and a chromobacteria. Other microbes found in the samples include Flavobacterium, Enterobacter, and several yeasts.

The limited aeration basin contained the curved bacteria found in the anaerobic lagoon in addition to those microbes identified in the aeration basin biological sludge. The population of the inactive facultative lagoon (40A-BIO-GRAB-5S) was too sparse to characterize under oil-immersion.

Most Probable Number (MPN) Results--Coliforms per 100 mℓ sample were:

40A-BIO-GRAB-1S:	No coliforms detected
40A-BIO-GRAB-2S:	No coliforms detected
40A-BIO-GRAB-3S:	MPN: 2.0×10^1 Confidence: $0.43\text{-}9.4 \times 10^1$
40A-BIO-GRAB-4S:	No coliforms detected
40A-BIO-GRAB-5S:	No coliforms detected

Subcultures of eosin methylene blue agar of 40A-BIO-GRAB-3S yielded typical Enterobacter sp. colonies.

Plate Count Results--(in terms of viable microbes per 1.0 mℓ sample):

40A-BIO-GRAB-1S:	3.3×10^7
40A-BIO-GRAB-2S:	8.2×10^7
40A-BIO-GRAB-3S:	2.0×10^6
40A-BIO-GRAB-4S:	7.0×10^7
40A-BIO-GRAB-5S:	3.8×10^6

Discussion of results--The microorganisms identified in the 40-Acre biological sludge are similar in type to the microbes found in domestic wastewater biological treatment. Dominant types of microorganisms isolated from domestic treatment plants include Achromobacter, Alcaligenes, Comomonas, Flavobacterium, Pseudomonas, Enterobacteriaceae, Thiobacillus, and Zoogloea (23, 57). This similarity of microbial type is most apparent in the aeration basin biological sludge microbes. Microbes identified in this aeration basin sludge include *Pseudomonas sp*., *Comamonas sp.*, *Enterobacter sp.*, Flavobacterium, and Zoogloea.

Previous studies have shown that microbes acclimate to a variety of wastes (122). Thus, the identification of similar microbial types between industrial and domestic wastewater treatment is not surprising.

Pseudomonas, a facultative anaerobe, was identified in the anaerobic lagoon sludge. However, the Pseudomonas isolated were feebly motile and not as vigorously motile as the Pseudomonas isolated from the aeration basins. In addition, large gram-positive yeast cells with budding were identified in the anaerobic lagoon sludge. Yeasts have been noted for the ability to metabolize certain organic substrates (153).

Phostosynthetic bacteria belonging to the family Thiorhodaceae were identified in the anaerobic lagoon. The strong, pink color of the anaerobic lagoon sample suggests a large population of the purple sulfur Thiorhodaceae: *Thiopedia rosea*. *Theopedia rosea* has been indicated as being responsible for reducing odor emissions from anaerobic lagoons (30). This microaerophilic bacteria uses hydrogen sulfide as the electron donor in photosynthesis and produces some type of oxidized sulfur compound as the end product. *Thiopedia rosea* has been isolated from West Coast anaerobic lagoons treating wastes from a large oil refinery and an animal fat rendering plant (30).

Washburn Tunnel Facility

The Washburn Tunnel Facility, a large high-rate activated sludge system, treats a flow of approximately 1.7×10^{5} m^{3}/day (45.0 MGD). The treatment process includes barscreening, grit removal, primary clarification, nutrient addition, pH control, activated sludge, and secondary clarification. Currently, sludge generated is dewatered in filter presses or centrifuges and barged to an off-site landfill. Plans call for incineration in the future.

During the sampling period Washburn Tunnel treated seven industrial waste streams, A through G, and discharges to the Houston Ship Channel. Section IV gives a more detailed site description.

For this study, Washburn Tunnel was sampled for four days, December 11 to 15, 1977. Characterization of the Washburn Tunnel wastewater and effluent loading values in kg/day (lb/day) for the sampling is presented in Table 102.

TABLE 100. CHARACTERIZATION OF WASHBURN TUNNEL WASTEWATER AND EFFLUENT LOADING IN KG/DAY (LB/DAY) FOR SAMPLING PERIOD

Wastewater Characteristic	Wastewater Loading		Effluent Loading		Percent Removal
Flow x 10^5 m^3/day (MGD)	1.7	(450)	1.6	(42.0)	
TOC	32,251	(70,952.2)	21,646	(47,621.2)	33
COD	266,905	(587,191)	76,066	(167,345.2)	72
BOD	49,511	(108,924)	6,835	(15,037)	86
TSS	146,448	(322,186)	19,144	(42,117)	87
NH_3-N	1,250	(2,750)	86.37	(190)	93
Phenol	144.9	(318.8)	11.59	(25.5)	92

Sampling Sites and Frequency--

The sampling program at Washburn Tunnel was designed to identify the fate of organic compounds in the treatment process and the active microbial populations present in the system.

Figure 54 shows the sites within the Washburn Tunnel Facility selected for sampling. Table 103 lists the organic and biological samples taken at the site, their location and sample identification designation.

Seven waste streams are treated at the facility. Five enter at influent point I (influents A through E) and two at Manhole #4 (influents F and G), as shown in Figure 54. Influents A through E (WT-ORG-COMP-I1) were composite sampled at a point past the bar screen in the grit chamber. The primary clarifier effluent (WT-ORG-COMP-I2) was composite sampled at the T-11 wet well. Because wastewater flow into the two primary clarifiers was equal, sampling of only one clarifier effluent was considered adequate. The effluents from the primary clarifiers combine with influents F and G at Manhole #4 before they enter the aeration basins (Figure 54). A composite sample was taken at the cooling tower wet well (WT-ORG-COMP-AI).

The final effluent sample (WT-ORG-COMP-E) was obtained from a GCWDA refrigerated composite sampler. This sampler collects approximately 8 to 10 effluent samples/day. Approximately 1.0 ℓ aliquots were taken from this final effluent sample and transferred to a single 4-ℓ bottle each day for the duration of the sampling period.

Grab samples of sludge were taken from the final clarifiers (WT-ORG-COMP-S16/17/27). The grab samples were adequate for obtaining samples from the aeration basins; however, problems were encountered in grab sampling at the final clarifiers. Determination of the sludge blanket level in the final clarifiers was both difficult and time-consuming. The use of submersible pumps (8 ℓ/min) to obtain the 1-ℓ sample solved the problem. A quick determination of the sludge blanket level could be made with the pumps, and rapid sampling was, therefore, possible.

Biological samples for microbial population studies were taken from four of the final clarifiers (T-16, T-17, 27A, and 27B) and the three aeration basins (T-19, T-20, and T-21). Both the grab sampler and the submersible pumps were used to obtain these samples.

Sediment samples for organic analyses were grabbed from the Houston Ship Channel using the La Motte Dredge. One sample was taken at the Washburn Tunnel effluent outfall (WT-ORG-GRAB-SED2) and another 180 m (600 ft) upstream from the outfall (WT-ORG-GRAB-SED1). Figure 54 shows the approximate location of these sampling stations.

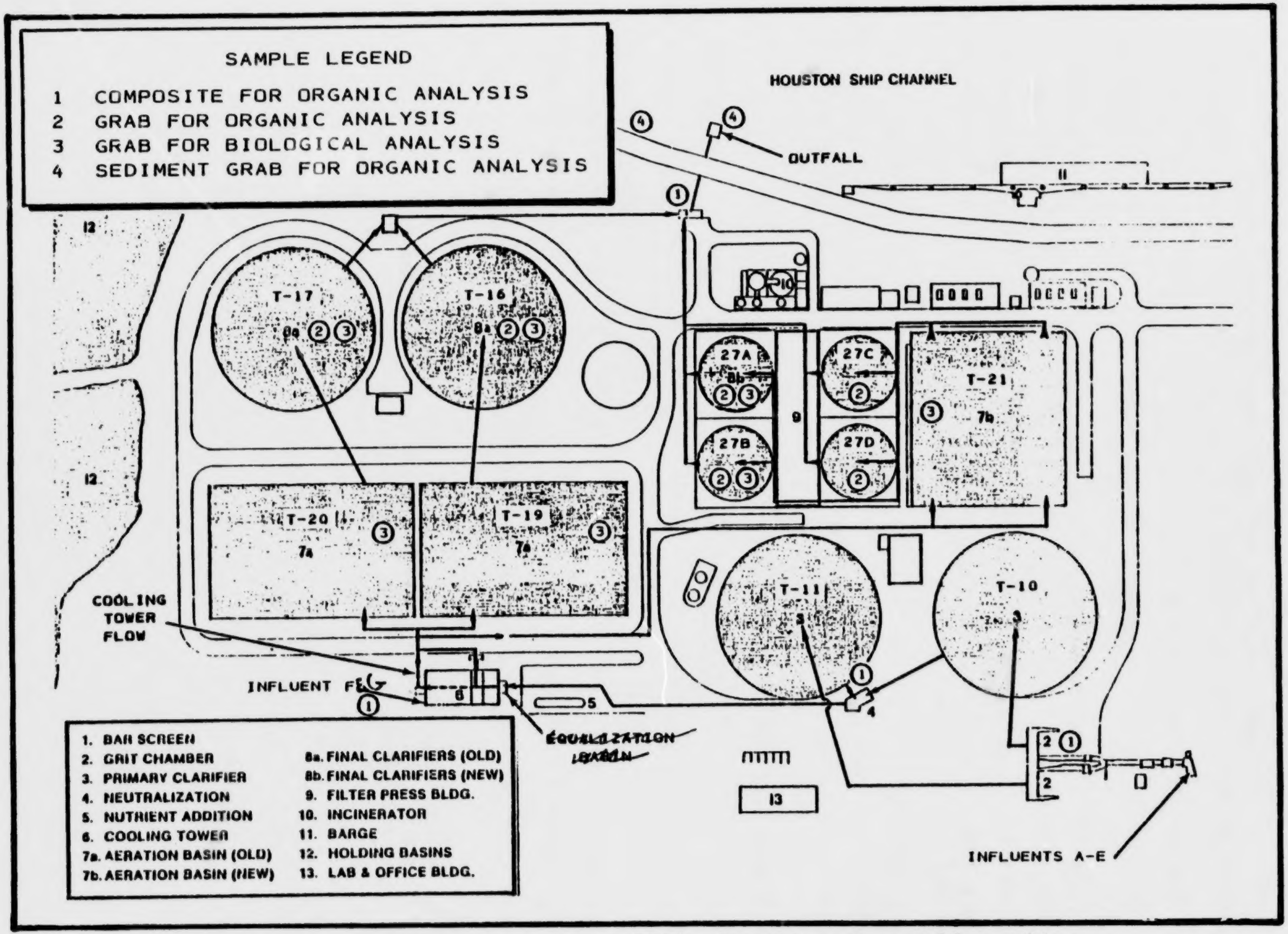
SAMPLE LEGEND
1 COMPOSITE FOR ORGANIC ANALYSIS
2 GRAB FOR ORGANIC ANALYSIS
3 GRAB FOR BIOLOGICAL ANALYSIS
4 SEDIMENT GRAB FOR ORGANIC ANALYSIS
HOUSTON SHIP CHANNEL
OUTFALL
T-17
T-16
T-20
T-19
T-21
T-11
T-10
27A
27B
27C
27D
8a
8b
7a
7b
COOLING TOWER FLOW
INFLUENT FL
EQUALIZATION BASIN
INFLUENTS A-E
1. BAR SCREEN
2. GRIT CHAMBER
3. PRIMARY CLARIFIER
4. NEUTRALIZATION
5. NUTRIENT ADDITION
6. COOLING TOWER
7a. AERATION BASIN (OLD)
7b. AERATION BASIN (NEW)
8a. FINAL CLARIFIERS (OLD)
8b. FINAL CLARIFIERS (NEW)
9. FILTER PRESS BLDG.
10. INCINERATOR
11. BARGE
12. HOLDING BASINS
13. LAB & OFFICE BLDG.

Figure 54. Washburn Tunnel facility layout and sampling sites.

TABLE 103. WASHBURN TUNNEL FACILITY ORGANIC AND BIOLOGICAL SAMPLE LOCATIONS AND IDENTIFICATION DESIGNATIONS

A. Samples for Organic Analysis

LOCATION	DESIGNATION
Influent for all wastes except Influent F&G	WT-ORG*-COMP*-I1
Primary Effluent	WT-ORG-COMP-I2
Influent to all aeration basins (after cooling tower)	WT-ORG-COMP-AI
Sludge from basins T-16, T-17, and 27 A to D	WT-ORG-COMP-S16/17/27
Plant effluent	WT-ORG-COMP-E
Sediment, upstream of outfall	WT-ORG-GRAB*-SED1
Sediment, at outfall	WT-ORG-GRAB-SED2

B. Samples for Biological Analysis

LOCATION	DESIGNATION
Aeration basin T-19	WT-BIO*-COMP-T-19
Aeration basin T-20	WT-BIO-COMP-T20
Aeration basin T-21	WT-BIO-COMP-T21
Sludge from T-16 and T-17	WT-BIO-GRAB-S2

*Notes.
ORG - organic analysis samples.
COMP - composite samples taken according to Sampling Methods.
BIO - biological samples for microbial analysis.
GRAB - grab samples taken according to Sampling Methods.

Chemical Analyses Results--

The results of the organic analyses of the samples taken at the Washburn Tunnel Facility are presented in Tables 104 through 106. The explanation of the sample designations used in these tables is given in Table 103 and shown in Figure 54.

Table 104 shows the organic chemical constituents present in the influent sources to the Washburn Tunnel, WT-ORG-COMP-I1, I2, and AI, and the effluent from the facility, WT-ORG-COMP-E. Tables 105 and 106 show the levels of similar organics present in the biological sludge from the final clarifiers (WT-ORG-COMP-S16/17/27) and the sediment samples obtained from the Houston Ship Channel (WT-ORG-GRAB-SED1 and SED2), respectively.

Discussion of Results--

Comparison of the concentrations of organic constituents in the Washburn Tunnel Facility influent-effluent (Table 104) shows assimilation of many groups of wastes, but not to the same degree as exhibited by the 40-Acre lagoon system. Removal, for the majority of the wastes, is approximately 50 percent, whereas the 40-Acre efficiency was 90 percent or greater. This suggests that retention time plays an important role in assimilation of hazardous organic materials. The retention time in activated sludge systems may not be adequate for biosorption. The short retention time in an activated sludge system may cause microbes to concentrate on the easier-to-degrade organics.

Groups of organics showing substantially greater than 50 percent removal (based on influent-effluent comparisons) were the halogenated aliphatics, ethers, and monocyclic aromatics. The 2, 4-dinitrotoluene was reduced from 390.0 μg/ℓ to below detection limits, and 4-bromophenyl phenyl ether was reduced from 258.0 to 0.2 μg/ℓ.

Phenol showed only a 26-percent reduction and 1, 2-diphenylhydrazine, a nitrosamine, a 28-percent reduction. Benzidine, also a nitrosamine, showed no influent-effluent reduction. Benzidine was reduced 75 percent in the 40-Acre lagoon system. Fluorene, which was reduced only 25 percent in the 40-Acre system, was reduced by 65 percent in the Washburn Tunnel system.

Historically, phenol has been removed 98 percent in the Washburn Tunnel treatment system (Table 75). The discrepancy between the removal efficiencies could be due to the differences in the phenol removal averaged for a year's sampling, whereas Table 104 reports removals for only a four-day sampling period.

The analysis for the Washburn Tunnel sludge (Table 105) shows a similar abundance of organic compounds as in the 40-Acre sludge. Certain of these compounds were found in high concentrations. Halogenated aliphatics (1, 2-dichloroethene, 1, 1, 1-trichloroethane, and tetrachloromethane) were found in the 2 to 5 mg/ℓ range.

TABLE 104. RESULTS OF GC ANALYSIS OF COMBINED EXTRACTS OF BASE/NEUTRAL AND ACID FRACTIONS ISOLATED FOR WASHBURN TUNNEL SAMPLES

(concentration values in μg/l, with no entry representing concentrations below detection limits)

Constituent	Sample (WT-ORG-COMP)			
	I1	I2	AI	E
Halogenated Aliphatics				
Hexachlorocyclopentadiene	-	29.0	113.0	-
Bis (2-chloroethoxy) methane	-	-	134.0	2.0
Ethers				
Bis (2-chloroisopropyl) ether	-	-	0.2	-
4-Bromophenyl phenyl ether	-	358.0	18.0	0.2
Bis (2-chloroethyl) ether	-	19.0	-	0.6
Monocyclic Aromatics				
1, 2, 4-Trichlorobenzene	-	-	28.0	-
2, 4-Dinitrotoluene	-	0.9	390.0	-
Phenols and Cresols				
2-Chlorophenol	-	0.1	0.9	-
2, 4-Dimethylphenol	-	-	15.0	-
2-Nitrophenol	-	-	9.0	-
Phenol	-	43.0	8.0	32.0
p-chloro-m-cresol	-	68.0	4.0	17.0
2, 4, 6-Trichlorophenol	-	4.0	-	-
Dichlorophenol	-	4.0	-	-
Phthalate Esters				
Dimethyl phthalate	-	-	2.0	1.0
Diethyl phthalate	1.5	0.6	6.0	3.0
Bis (2-ethylhexyl) phthalate	-	1.0	2.0	0.9
di-n-butyl phthalate	-	2.0	-	-
Butyl benzyl phthalate	30.0	-	-	-
Polycyclic Aromatic Hydrocarbons				
Naphthalene	-	1.2	4.0	2.0
Acenaphthylene	-	0.4	1.0	0.2
Acenaphthene	0.6	1.0	1.0	0.5
Fluorene	-	-	280.0	98.0
Phenanthrene	-	0.9	1.0	1.0
Fluoranthene	-	2.0	2.0	1.0
Pyrene	-	3.0	9.0	5.0
Benzo(a) pyrene	17.0	-	-	-
Benzo(a) anthracene	76.0	-	-	-
Benzo(b) fluoranthrene	5.0	-	-	-

TABLE 104 (continued)

Constituent	Sample (WT-ORG-COMP-) I1	I2	AI	E
Nitrosamines and Other N-Compounds				
1, 2-Diphenylhydrazine	-	247.0	341.0	244.0
Benzidine	1.6	4.0	4.0	4.0
PCB's and Related Compounds				
2-Chloronaphthalene	-	2.0	1.0	0.2
Pesticides				
Isophorone	-	0.2	-	-

TABLE 105. RESULTS OF GC/MS ANALYSIS OF WASHBURN TUNNEL SLUDGE SAMPLES WT-ORG-COMP-S16/17/27

(concentration values in μg/l)

Constituent	Concentration
Halogenated Aliphatics	
1, 2-Dichloroethene	2,900.0
1, 3-Dichloro-1-propene (trans)	145.0
1, 3-Dichloro-1-propene (crs)	31.0
Trichloroethene	18.0
1, 1, 1-Trichloroethane	5,490.0
Tetrachloromethane (carbon tetrachloride)	2,375.0
Monocyclic Aromatics	
Benzene	1,233.0
Toluene	233.0
2, 4-Dintrotoluene	2.0
2, 6-Dintrotoluene	0.5
Phenols and Cresols	
2, 4, 6-Trichlorophenol	
2, 4-Dimethylphenol	0.9
2-Chlorophenol	0.5
Phenol	0.5
p-chloro-m-cresol	1.0
Phthalate Esters	
Diethyl phthalate	0.5
Dioctyl phthalate	20.0
Polycyclic Aromatic Hydrocarbons	
Acenaphthylene	0.5
Acenaphthene	0.5
Fluoranthene	1.0
Nitrosamines and Other N-Compounds	
Benzidine	1.0
PCB's and Related Compounds	
2-Chloronaphthalene	0.5
Pesticides	
Isophorone	1.0

TABLE 106. RESULTS OF GC AND GC/MS ANALYSES OF
WASHBURN TUNNEL SEDIMENT SAMPLE
(concentration values in ng/Kg dry weight, with no entry representing
concentrations below detection limits)

Constituent	Sample (WT-ORG-GRAB-)	
	SED1	SED2
Halogenated Aliphatics		
Dichloromethane	959.0	1,964.0
1, 1-Dichloroethene	8.0	0.2
1, 2-Dichloroethene	3.0	-
Trichloromethane (chloroform)	310.0	258.0
1, 3-Dichloro-1-propene	1.0	-
Trichloroethene	2.0	0.9
1, 1, 2-Trichloroethane	2.0	1.4
1, 1, 22-Tetrachloroethane	1.0	2.0
Hexachlorocyclopentadiene	-	106.0
Ethers		
4-Bromophenyl phenyl ether	1,056.0	69.0
Bis (2-chloroethyl) ether	1,940.0	-
Monocyclic Aromatics		
Benzene	63.0	15.0
Toluene	4.0	-
Nitrobenzene	65.0	-
2, 4-Dinitrotoluene	1,379.0	46.0
Phenols and Cresols		
2-Nitrophenol	86.0	-
2-Chlorophenol	56.0	-
Phenol	345.0	115.0
p-chloro-m-cresol	1,250.0	-
2, 4, 6-Trichlorophenol	560.0	115.0
Phthalate Esters		
Dimethyl phthalate	-	106.0
Diethyl phthalate	267.0	138.0
Di-n-butyl phthalate	323.0	-
Polycyclic Aromatic Hydrocarbons		
Naphthalene	103.0	59.0
Acenaphthylene	474.0	37.0
Acenaphthene	647.0	115.0
Fluorene	1,293.0	321.0
Phenanthrene	-	92.0
Fluoranthene	496.0	298.0
Benzo(a) pyrene	216.0	46.0

TABLE 106 (continued)

Constituent	Sample (WT-ORG-GRAB-) SED1	SED2
Nitrosamines and Other N-Compounds		
Benzidine	517.0	505.0
1, 2-Diphenylhydrazine	2,112.0	367.0
Pesticides		
Isophorone	483.0	206.0

Monocyclic aromatics benzene and toluene were 1,233.0 and 233.0 μg/ℓ, respectively. None of these organics were identified in the Washburn Tunnel influent-effluent. The high concentrations of these organics in the sludge suggests that they are recalcitrant compounds.

The remaining organics in the sludge were all below 50 g/ℓ in concentration. The 2, 4-dinitrotoluene was reduced from 390.0 μg/ℓ in the influent and was below the detection limits in the effluent. The sludge concentration was 2.0 μg/ℓ, suggesting biooxidation of 2, 4-dinitrotoluene or the removal of the nitro groups and conversion of the compound to toluene (233.0 μg/ℓ in the sludge). This is also true for the ethers. Ethers are relatively volatile compounds and may be air-stripped in the aeration basis. None of the ethers identified in the wastewater were found in the sludge.

The fluorene concentration was lowered by 65 percent in the treatment system, from 280.0 to 98.0 μg/ℓ. Fluorene was not identified in the sludge, a contradiction to the fluorene concentration in the 40-Acre sludge, where fluorene was a major constituent.

The sediment grabbed from the Houston Ship Channel at and near the Washburn Tunnel outfall was a black, viscous material, with a strong smell of oil. The Houston Ship Channel carries a high volume of ship traffic and has a number of water-using industries located along its shores. Consequently, it is impossible to confirm the origin of the organics identified in the sediments. This is apparent when the upstream sediment concentrations are compared to the outfall sediment concentrations (Table 106). The sample grabbed upstream of the Washburn Tunnel outfall, WT-ORG-GRAB-SED1, has a greater concentration than the outfall sample. Therefore, it is not possible to attribute any of the conditions observed in the receiving environment exclusively to the Washburn Tunnel operation.

The data illustrate the affinity of clay sediments for organics. Many organic compounds were identified in the sediment, with concentrations in the mg/ℓ range.

Biological Analyses Results--

Wet mount, gram-stain, and identification summary--Flora was qualitatively uniform throughout. Gram-negative organisms were dominant, comprising over 95 percent of the cells observed. The gram-positive forms observed were primarily cocci with an occasional yeast. A few unicellular algae and debris, possible fungal hyphae, were also identified.

The predominant organisms seemed to be gram-negative, vigorously motile rods about 1.5 x 0.5 micra, mostly single but some in pairs (*Pseudomonas sp*.). Stalked, gram-negative bacteria (*Caulobacter sp.*) were very common and were attached to flocs of debris and bacteria. Other bacteria found included a gram-negative, short, plump, rod staining uniformly and densely, mostly single but some in pairs and rare chains (Chromobacteria, red-orange pigmented), and a gram-negative bacterial filament of about 1 x 40 to 80 micra in length (*Arthrobacter sp.*).

The WT-BIO-COMP-T20 sample yielded *Thiobacillus ferrooxidans*, although all samples contained thiosulfate-oxidizing autotrophs and possibly ammonia-oxidizing bacteria.

Other common microbes found in the samples included Flavobacterium, Enterobacter, and several yeasts (not characterized).

Most probable number (MPN) results--Coliforms per 100 mℓ sample were:

WT-BIO-COMP-T19: MPN: 2.5×10^5 Confidence: $0.38\text{-}16.0 \times 10^5$
WT-BIO-COMP-T20: MPN: 6.0×10^4 Confidence: $0.91\text{-}40.0 \times 10^4$
WT-BIO-COMP-T21: MPN: 2.5×10^5 Confidence: $0.38\text{-}16.0 \times 10^5$
WT-BIO-GRAB-S2: MPN: 1.3×10^5 Confidence: $7.0\text{-}86.0 \times 10^4$.

Subcultures of eosin methylene blue agar revealed colonies typical of *Enterobacter aerogenes*. No *Escherichia coli* was detected.

Plate count results--(In terms of viable microbes per 1.0 mℓ):

WT-BIO-COMP-T19: 1.35×10^7
WT-BIO-COMP-T20: 8.1×10^6
WT-BIO-COMP-T21: 5.0×10^7
WT-BIO-GRAB-S2: 6.2×10^7.

Discussion of results--The microflora identified in the Washburn Tunnel biological sludge are comparable to the microflora common to domestic activated sludge sewage treatment. The exception, *Escherichia coli*, a microbe ubiquitous in domestic sewage, was not isolated from the sludge. The absence of an enteric bacteria is not unusual; Washburn Tunnel handles no sanitary wastes.

Pseudomonas, the predominate microbe isolated from the sludge, has been noted previously as being the dominant organism in treating carbohydrate-rich wastes (57). The predominance of Pseudomonas in the Washburn Tunnel activated sludge is an indication of the ability to acclimate to various organic substrates, both domestic and industrial.

A major waste source (60 to 70 percent) to the Washburn Tunnel is a kraft paper mill effluent. A recent study has indicated the association of coliform bacteria, specifically Klebsiella, of nonfecal origin with pulp mill wastes (83). This study found MPN results of 10^5 cells per 100 mℓ for coliform bacteria. Selective media growth tests were performed on isolates from the MPN tests with eosin methylene blue agar. These tests revealed colonies typical of Enterobacter aerogenes. The results of the two studies, the association of high numbers of coliform bacteria with paper manufacturing effluent, suggest coliform bacteria assimilation of wood pulp wastes. Yeasts, which were also isolated from the sludge, have been noted for removal of resins from kraft mill effluents (153).

The iron-oxidizing bacteria, Thiobacillus ferroxidans, was isolated from the biological sludge. In addition, all samples contained thiosulfate-oxidizing autotrophs and possibly ammonia-oxidizing bacteria.

ECO Deep Shaft Facility

The Deep Shaft treatment plant in Paris, Ontario, Canada is a pilot system. It treats a portion of the wastewater received at a conventional extended aeration wastewater treatment plant operated by the Ontario Ministry of the Environment. The Deep Shaft Facility is capable of treating 473 m^3/day (0.12 MGD) of difficult-to-treat industrial/domestic blends. The industrial waste components come from 14 sources, the major source a textile plant. Total retention time is 30 min.

The Deep Shaft Facility, a secondary biological process, uses a totally enclosed subsurface aeration shaft. Fluid pressure with depth creates increased oxygen solubility and enhances oxygen transfer efficiency.

Deep Shaft was sampled for five days March 13 to 17, 1978. During the sampling period, the wastewater treatment scheme consisted of bar screening, comminutor, acid neutralization, deep shaft biooxidation, air flotation, and discharge to the main plant. Characteristics of the influent and effluent loading values for conventional parameters during the sampling period are presented in Table 107.

Sampling Sites and Frequency--

Figure 55 shows the sites selected for sampling at the Deep Shaft Facility. Table 108 presents a list of the organic and biological samples taken, their location, and the sample identification designation. The following discussion explains the selection of the sampling sites.

Samples for organic analysis were taken at various points in the system. The influent sample (DS-ORG-COMP-I) was obtained

TABLE 107. CHARACTERIZATION OF THE DEEP SHAFT WASTEWATER AND EFFLUENT LOADING IN KG/DAY (LB/DAY) FOR THE SAMPLING PERIOD

Wastewater Characteristic	Wastewater Loading		Effluent Loading		Percent Removal
Flow x 10^2 m^3/day (MGD)	4.5	(0.12)	4.5	(0.12)	
Total BOD_5	82	(181)	15	(33)	82
Soluble BOD_5	33	(73)	6	(13)	82
COD_5	403	(888)	90	(198)	78
SS	140	(309)	27	(60)	81

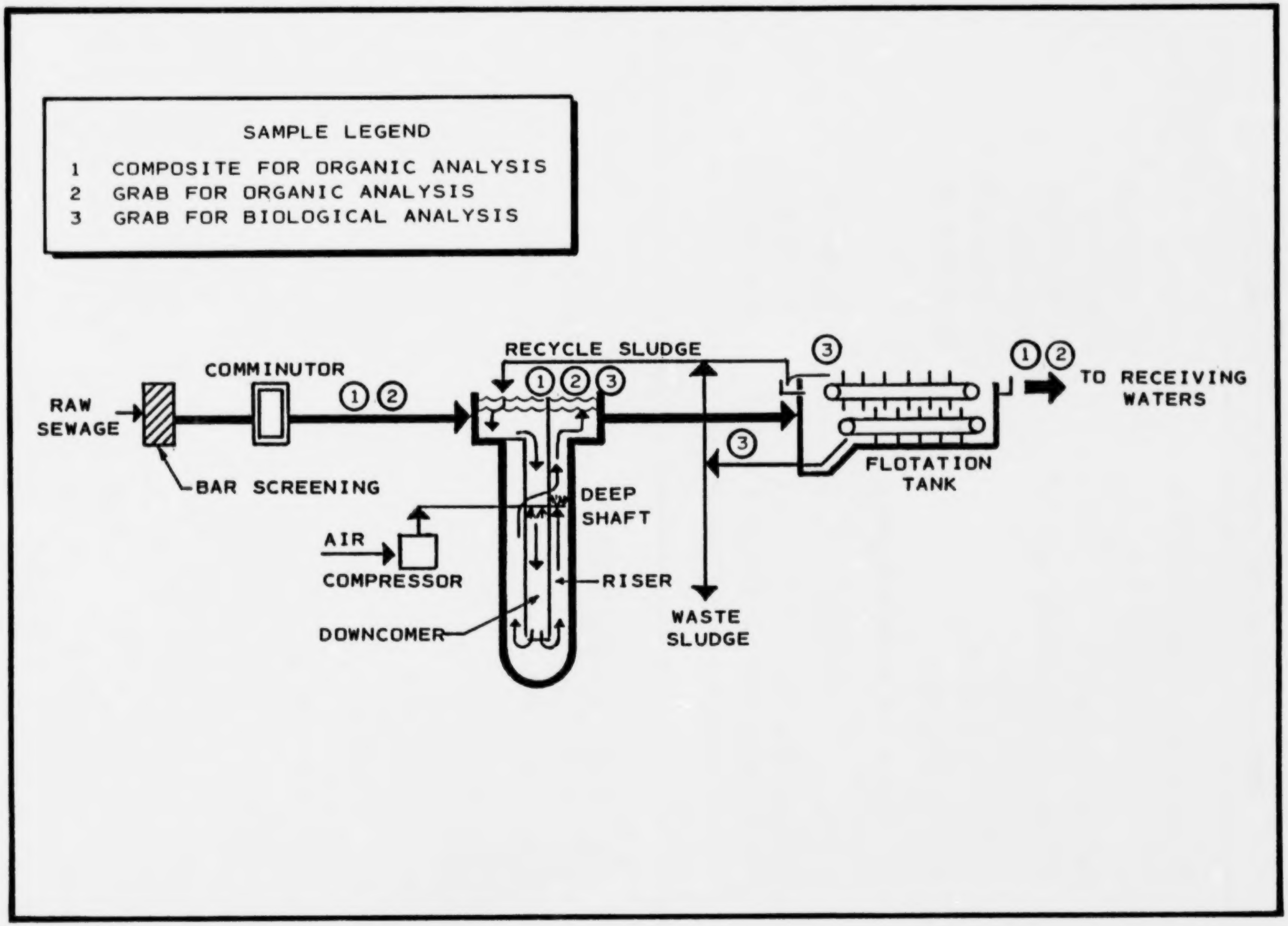
SAMPLE LEGEND
1 COMPOSITE FOR ORGANIC ANALYSIS
2 GRAB FOR ORGANIC ANALYSIS
3 GRAB FOR BIOLOGICAL ANALYSIS
RAW SEWAGE
BAR SCREENING
COMMINUTOR
① ②
RECYCLE SLUDGE
① ② ③
AIR
COMPRESSOR
DEEP SHAFT
RISER
DOWNCOMER
③
WASTE SLUDGE
③
FLOTATION TANK
① ②
TO RECEIVING WATERS

Figure 55. Paris Deep Shaft Facility.

TABLE 108. DEEP SHAFT FACILITY ORGANIC AND BIOLOGICAL SAMPLE LOCATIONS AND IDENTIFICATION DESIGNATIONS

A. Samples for Organic Analysis

LOCATION	DESIGNATION
Influent to shaft	DS-ORG*-COMP*-I
Effluent from flotation tank	DS-ORG-COMP-EF
Influent to shaft	DS-ORG-GRAB-I
Effluent from shaft	DS-ORG-GRAB-SEF
Waste mixed liquor	DS-ORG-COMP-WS

B. Samples for Biological Analysis

LOCATION	DESIGNATION
Effluent from shaft	DS-BIO*-GRAB*-SEF
Bottom sludge from air flotation tank	1-DS-BIO-GRAB-WS
Floated sludge from air flotation tank	2-DS-BIO-GRAB-WS

*Notes.
ORG - organic analysis samples.
COMP - composite samples taken according to Sampling Methods.
BIO - biological samples for microbial analysis.
GRAB - grab samples taken according to Sampling Methods.

from a refrigerated composite sampler (Sirco). The effluent sample (DS-ORG-COMP-E) was obtained with a composite sampling set-up developed for this study. The composite sampler was also used to obtain the waste sludge sample (DS-ORG-COMP-WS) from the head tank of the shaft. During the sampling period, 1-ℓ aliquots were taken from 4-ℓ composite samplers and composited into single 4-ℓ bottles daily.

Grab samples for organic analysis were taken from the influent (DS-ORG-GRAB-I) and shaft effluent (DS-ORG-COMP-SEF). The influent sample was obtained from a draw-off spigot on the influent pipe from the surge tank, the shaft effluent sample from the spigot on the shaft effluent pipe from the riser to the flotation tank.

Biological samples for the microbial population study were grabbed from the shaft effluent (DS-BIO-GRAB-SEF), the air flotation tank bottom sludge (1-DS-BIO-GRAB-WS), and the air flotation tank-floated sludge blanket (2-DS-BIO-GRAB-WS). The shaft effluent sample was drawn from a spigot on the shaft effluent pipe from the riser to the flotation tank.

Chemical Analyses Results--

The results for the organic analyses of the Deep Shaft Facility are presented in Tables 109 and 110. An explanation of sample designations used in these tables is given in Table 108.

Table 109 shows the organic chemical constituents detected by composite sampling of the shaft influent (DS-ORG-COMP-I), the effluent from the entire system (DS-ORG-COMP-EF), and the waste mix liquor from the shaft (DS-ORG-COMP-WS). Table 110 shows the levels of similar organics detected in the grab samples taken from the shaft influent (DS-ORG-GRAB-I) and the effluent from the shaft (mixed liquor) (DS-ORG-GRAB-SEF) during a peak dye discharge.

Sludge at this Deep Shaft pilot plant is wasted from both the floated and bottom sludge from the air flotation tank. Therefore, to obtain a representative sampling of total sludge, a sample of the mixed liquor was taken from the shaft head tank. The percent solids by weight of this sample was 0.56 percent.

Discussion of results--Comparison of influent-effluent and waste sludge concentration values (Table 109) shows a variety of organics in each sample. Influent chloroform concentration is 22.0 mg/ℓ, the sludge concentration is 1.9 mg/ℓ, and the effluent concentration is below detection limits. Carbon tetrachloride influent concentration is 2.2 mg/ℓ, and the effluent and waste sludge concentrations are below detection limits. Volatilization of these organics may be a major removal pathway. Chloroform inhibits bacterial cell multiplication at concentrations

TABLE 109. RESULTS OF GC AND GC/MS ANALYSES OF
DEEP SHAFT COMPOSITE SAMPLES
(concentration values in µg/l, with no entry representing
concentrations below detection limits)

	Sample (DS-ORG-COMP-)		
Constituent	I	EF	WS
Halogenated Aliphatics			
Dichloromethane	-	-	20.0
Trichloromethane (chloroform)	22,000.0		1,938.0
Tetrachloromethane (carbon tet.)	2,185.0	-	-
1, 1, 2-Trichloroethane	11.0	-	-
Tetrachloroethene	5.0	-	1.0
1, 1, 2, 2-Tetrachloroethane	8.0	-	3.0
Trichloroethene	18.0	-	1.0
1, 3-Dichloro-1-propene	-	-	235.0
Monocyclic Aromatics			
Benzene	336.0	-	14.0
Toluene	30.0	-	5.0
1, 2, 4-Trichlorobenzene	5.0	-	34.0
Chlorobenzene	-	100.0	-
2, 4-Dinitrotoluene	-	100.0	500.0
2, 6-Dinitrotoluene	-	200.0	700.0
Nitrobenzene	-	-	100.0
Phenols and Cresols			
Phenol	18.0	-	15.0
2, 4-Dimethylphenol	-	-	150.0
2-Chlorophenol	-	100.0	-
2, 4, 6-Trichlorophenol	-	-	1,000.0
Pentachlorophenol	-	-	1,000.0
Phthalate Esters			
Dimethyl phthalate	70.0	200.0	-
Dioctyl phthalate	1,000.0	5,000.0	2,010.0
Polycyclic Aromatic Hydrocarbons			
Acenaphthene	180.0	-	41.0
Anthracene	-	500.0	-
Chrysene	-	100.0	-
Phenanthacene	-	-	2,000.0
Benzo(a) pyrene	-	-	1,000.0
Nitrosamines			
Benzidine	-	200.0	-

TABLE 109 (continued)

Constituent	Sample (DS-ORG-COMP-) I	EF	WS
Pesticides			
Isophorone	7.0	-	-
Chlordane*	-	-	0.2
DDD*	-	-	0.1
Alkyl stannane	-	-	< 10.0
Monochloroalkyl stannane	-	-	< 10.0
Hexadecanoic acid (Palmic acid)	-	-	>100.0

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*Both GC-ECD assignments unconfirmable by GC/MS due to low levels. Due to banned status of chlordane and DDD's precursor (DDT) in Canada, assignments are doubtful.

TABLE 110. RESULTS OF CG AND GC/MS ANALYSES OF DEEP SHAFT GRAB SAMPLES

(concentration values in μg/l, with no entry representing concentrations below detection limits)

Constituent	Sample (DS-ORG-GRAB-) I	SEF
Halogenated Aliphatics		
Dichloromethane	-	13.0
Trichloromethane (chloroform)	-	2,309.0
1, 1, 2-Trichloroethane	-	1.0
1, 3-Dichloro-1-propene (trans)	-	66.0
1, 3-Dichloro-1-propene (cis)	-	4.0
1, 1-Dichloroethene	-	3.0
Monocyclic Aromatics		
Benzene	-	193.0
Toluene	-	26.0
Trichlorobenzenes	-	1,000.0
Chlorobenzene	10.0	-
Nitrobenzene	-	300.0
Phenols and Cresols		
Phenol	1,000.0	1,500.0
2-Chlorophenol	10.0	-
Dinitrophenol	-	100.0
2, 4, 6-Trichlorophenol	-	500.0
p-chlorocresol	-	1,000.0
Pentachlorophenol	-	1,000.0
Phthalate Esters		
Dimethyl phthalate	-	1,000.0
Diethyl phthalate	-	1,000.0
Dioctyl phthalate	2,000.0	10,000.0
Polycyclic Aromatic Hydrocarbons		
Acenaphthene	-	100.0
Dibenzo(g,h,i) perylene	50.0	-
Benzo fluoranthene	700.00	-
Benzo(a) pyrene	200.0	4,000.0
Pesticides		
Chlordane	-	100.0

greater than 125 mg/ℓ and carbon tetrachloride inhibits it at concentrations greater than 30 mg/ℓ (163). In addition, the alkyl stannanes identified are newly developed compounds that are effective biostats and are added to surface paints to restrict fungal or mold growth. The use of these chemicals in an aqueous medium is banned in the United States, but their status in Canada is now known. It is also not known if the concentrations determined in the waste sludge (<10.0 μg/ℓ) are biocidal.

The chloroform, carbon tetrachloride, and stannanes may be limiting factors to the assimilative capacities of the Deep Shaft. The assimilation of BOD and other wastewater pollutant parameters by the Deep Shaft may improve when the influent concentrations of these chemicals is limited.

Biological Analyses Results--

Wet mount, gram-stain, and identification summary--The shaft effluent (DS-BIO-GRAB-SEF) contained mainly gram-negative, vigorous, motile rods and cocco-bacillus. The most common organism found was a small, motile, gram-negative rod that occurred singly and in pairs (*Pseudomonas sp.*). Stalked gram-negative bacteria (*Caulobacter sp.*) were found attached to flocs, which were composed of gram-negative material. Very small gram-negative cocci (*Micrococcus sp.*) were found singly or in pairs. Occasional large, blunt, gram-positive rods (*Bacillus sp.*) were found associated with the flocs.

The air flotation tank floated sludge (2-DS-BIO-GRAB-WS) contained mostly small, motile, gram-negative rods. A few gram-positive rods and cocci were associated with the gram-negative floc-bacteria complexes. The flotation tank bottom sludge (1-DS-BIO-GRAB-WS) contained small motile gram-negative rods, gram-negative coccibacilli, and larger, gram-negative, blunt, dense, staining bacilli (*Desulfovibrio desulfuricans* and/or *Thiobacillus sp.*).

Other common microbes found in the samples were *Escherichia coli*, *Enterobacter aerogenes*, *Pseudomonas fluorescans*, *Flavobacterium sp.*, chromobacteria (red-orange-pink), sulfur oxidizers (*Thiobacillus sp.*), yeasts, and a streptomycete.

Most probable number (MPN) results--Coliform per 100 mℓ sample:

DS-BIO-GRAB-SEF:	MPN:	1.5×10^6	Confidence	$3.2\text{-}70.0 \times 10^6$
1-DS-BIO-GRAB-WS:	MPN:	4.5×10^6	Confidence	$1.0\text{-}12.0 \times 10^6$
2-DS-BIO-GRAB-WS:	MPN:	2.5×10^5	Confidence	$0.5\text{-}12.0 \times 10^5$.

Plate count results--Microbes per 1.0 mℓ sample:

DS-BIO-GRAB-SEF: 1.2×10^9
1-DS-BIO-GRAB-WS: 5.9×10^9
2-DS-BIO-GRAB-WS: 8.5×10^8.

Discussion of results--The Paris Deep Shaft Facility treats a 70:30 industrial/domestic wastewater blend; the biological seed originates at the adjacent municipal wastewater treatment facility. Consequently, the flora at the Deep Shaft Facility is similar to that of a municipal biological sludge.

A Pseudomonas bacteria was the most common organism found in the effluent. This compares to the predominance of Pseudomonas in the activated sludge and lagoon system biological sludges. In addition, other organisms included enteric bacteria, a fungi, yeasts, and sulfur oxidizing bacteria.

Biological analyses were performed on the air flotation tank floated sludge and the bottom return sludge to compare the flora associated with each sludge. The floated sludge contained mainly Pseudomonas associated with floc-bacteria complexes. The bottom return sludge contained Pseudomonas, Micrococcus, and Bacillus bacteria, and a gram-negative, dense-staining bacilli identified as *Desulfovibrio desulfuricans* or a Thiobacillus. Both bacteria are sulfur-oxidizing bacteria. These normally autotrophic organisms have been known to metabolize organic compounds (109).

The plate count results were 100 to 1,000 times greater than the actual sludge or lagoon system plate count results, this reflecting the higher MLVSS concentration maintained in the shaft.

SECTION VI

ENGINEERING AND ECONOMIC COMPARISONS OF IDENTIFIED BIODEGRADATION TECHNIQUES

INTRODUCTION

The purpose of this section is to provide design, performance, and economic comparisons and evaluations of the biological treatment technologies presented in Section IV and Section V of this report. The applicability of conventional and innovative biological treatment methods described in Section III to various problematic wastes is also discussed.

The objectives of technology comparisons and discussions are as follows:

- To identify robust biological treatment techniques, within defined environmental and waste constraints, applicable to a variety of organic materials
- To identify those treatment characteristics which enhance biodegradation of problematic wastes, so that they may be more widely applied
- To compare potential secondary impacts on the environment, including accumulated organic wastes in sludge materials
- To evaluate the economic factors associated with each treatment technology, so that effectiveness per unit cost can be maximized.

It is emphasized that results of comparisons made in this report are subject to the manner in which evaluation criteria are weighed. Some of these evaluation criteria, in turn, require comparative rather than absolute consideration. For example, when four types of biodegradation technologies are evaluated according to land requirements, the results are relative to the technologies considered. This does not mean that the low-rated technology is land intensive, based on comparison with the average land requirements of the universe of treatment technologies. Special mention is also made of the fact that technology ratings presented in this section imply that conditions actually existed at the sites described in Sections IV and V.

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METHODS FOR COMPARING TREATMENT TECHNOLOGIES

The approach to comparisons of studied technologies is shown in Figure 56. General groups of criteria are first defined, based on the objectives of the study. Specific comparative criteria are then defined within each group, and applied to the considered technologies.

General Criteria Groups

The criteria for making engineering and economic comparisons of biodegradation technologies are included under three general groups:

- Design
- Performance
- Economics.

Specific Criteria

Specific criteria included in these groups are listed in Table 111. Most criteria are self-explanatory and were developed to provide industrial engineers with useful descriptions of each considered technology.

The variety of construction required (Table 111: Part I, Item 5) refers to the relative sophistication of each technology. Activated sludge treatment processes, for instance, usually require provisions for fabricated clarifier basins, sludge rakes, and sludge pumping and transfer plumbing. In contrast, some lagooning operations require relatively few construction activities for installation.

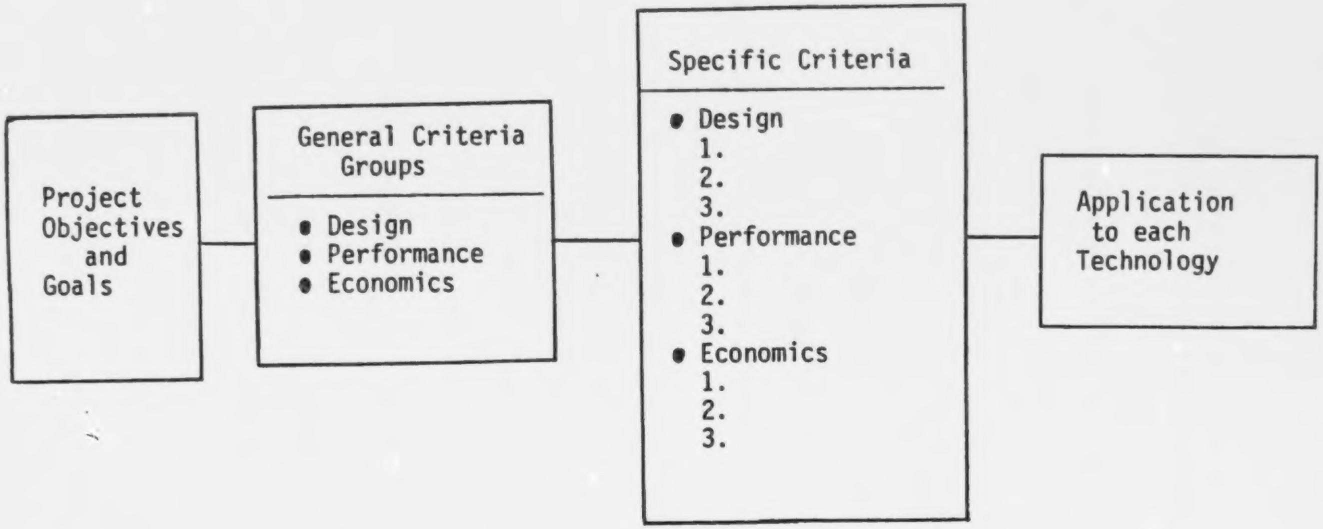
Project Objectives and Goals
General Criteria Groups
• Design
• Performance
• Economics
Specific Criteria
• Design
1.
2.
3.
• Performance
1.
2.
3.
• Economics
1.
2.
3.
Application to each Technology

Figure 56. Approach to comparisons of studied technologies.

TABLE 111. SPECIFIC DESIGN, PERFORMANCE AND ECONOMIC CRITERIA FOR COMPARING BIODEGRADATION TECHNOLOGIES

Part I. Design

1. Scale: Estimated range of system sizes which may be applied to wastewater stream of similar composition and result in unimpaired treatment performance.
2. Controlling waste stream design parameters and functions well defined.
3. Availability of data on effects of variations in standard design.
4. Detailed designs and specifications readily available.
5. Variety of construction required.
6. Serviceability of primary system components.
7. Provisions for backup or standby equipment.
8. Provisions for spill basins to divert unacceptable concentrated or toxic wastes without bypassing untreated to receiving waters.
9. Possible risk of groundwater contamination under certain soil and geological conditions.
10. Flexible sludge return and/or wasting capacities.
11. Internal system flexibility (e.g. routing of waste flows can be varied).
12. Flow equalization (e.g. storage of wastes prior to treatment) required.
13. Design favors microbial populations which are well adapted for reduction of problematic industrial organic wastes.
14. System readily operated-automated.
15. Unit processes capable of being sheltered.
16. Ease of construction in varying terrains.
17. Potential for impact on air quality.
18. Potential for impact on visual esthetics (can or cannot be located near urbanized areas).
19. Amenability of existing design to additions or modifications for upgrading or increase in capacity.

Table 111 (continued)

Part II. Performance

1. Conventional removals.
2. Meeting NPDES limits on current treatment standards.
3. Range of treatable organic wastes.
4. Degree of biotransformation:

$$\frac{\text{amt. in effluents + amt. in sludges}}{\text{amt. in influents}} \times 100$$

5. Susceptibility to certain organic toxins.
6. Susceptibility to certain inorganic toxins.
7. Susceptibility to shock loading (concentrated wastes).
8. Rate of O_2 transfer.
9. Amount of secondary sludge produced/Kg. of BOD removed.
10. Ease of sludge handling-dewatering.
11. Minimum and maximum tolerable flowrates.
12. Minimum and maximum tolerable loading rates.
13. Incidental removal of non-oxygen demanding materials (metals, salts, etc.).
14. Accumulation of discharged organic materials in receiving waters.
15. Susceptibility to variations in air temperature.

Part III. Economic

1. Land required relative to other technologies treating similar waste stream flows.
2. Engineering design costs.
3. Costs of construction (earth moving and erection of structures). Capital expenses for "off-the-shelf" equipment and installation, and expected salvage value.
4. Maintenance costs.

Table 111 (continued)

5. Supervision and labor costs.
6. Chemical costs.
7. Energy costs - (electricity and fuel).
8. Total cost amortized over expected lifetime and expressed in terms of kilograms of various removed constituents.
9. Cost increases with increased scales.
10. Costs of ultimate disposal of secondary wastes (air, emmisions, and sludge).

Serviceability of system components (Part I, Item 6) refers to several factors, including ease of access to components, man-hours and level of training required for maintenance personnel. Provisions for backup or standby equipment (Part 1) and spill basins (Part 1) refers to the amenability of the treatment technology to installation of such equipment. It does not imply the presence or absence of such equipment at the specific case study sites described in Section IV.

The "conventional removals" criteria listed in Part II refers to the reduction of the following waste parameters discussed in Section IV:

Total Organic Carbon (TOC)
Chemical Oxygen Demand (COD)
Biological Oxygen Demand (BOD)
Total Suspended Solids (TSS)
Volatile Suspended Solids (VSS)
Total Dissolved Solids (TDS)
Chloride
Sulfide
Phosphorus
Total Nitrogen
Various Metals
Oil and Grease.

The "range of treatable organic wastes" applies to reduction of specific organic waste constituents reported in Section V of this report.

The estimated degree of biotransformation of organic waste materials (Part II, Item 4) is important because it considers the potential for accumulations of recalcitrant organic compounds in sludges. Total biotransformation is, then, taken to be the ratio of effluent sludge waste concentrations to the influent concentrations. Waste accumulations in sludges may result in environmental problems at land disposal or incinerator facilities.

The susceptibility to organic or inorganic toxins or shock loading (Part II, Items 5, 6, and 7) indicate system stability under varying waste conditions. Shock loading is differentiated from fluctuations in toxin content in that the former can be caused by high concentrations (e.g., extremely high COD or BOD) of organic compounds which are not detrimental to the plant biota in usual and expected concentrations. Toxins, on the other hand, are wastes which are not usually present or present only in dilute concentrations which increase in concentration unexpectedly.

COMPARISONS OF CASE STUDY TECHNOLOGIES

Design

Both the pure oxygen UNOX and Deep Shaft systems were found to be equally superior from a design standpoint. This is due primarily to controlled sludge production, favoring of accelerated microbial metabolism through innovative techniques, and the fact that both systems are closed and relatively compact. They are also easily supervised and readily adaptable to a variety of terrains. Unique positive design attributes of Deep Shaft technology include excellent sludge control and minimization of sludge production, ease of system automation, and minimal impact on visual aesthetics and air quality. The UNOX system had almost the same positive attributes. UNOX is somewhat more difficult to house and protect from colder air temperatures, but is not as dependent upon proper site selection based on geological characteristics.

Performance

All monitoring and special testing data for organic waste reduction, as evidenced in this report, indicate that the series lagoon system was superior to other treatment methodologies in removing the broadest range of organics with the highest level of biodegradation. The lagoon system was also superior in terms of sustaining shock loadings and large fluctuations in flow rates. Lagoons did not measure up to other techniques only in the rate of O_2 transfer and impact of air temperature.

Economic

Series lagoon systems are most desirable in terms of economic criteria. Series lagoons are found to be above average for all specific cost criteria except land requirements and cost variations with scale.

Under conditions where land is extremely expensive or not available, or where smaller flow rates are involved (less than 1 MGD), the most attractive alternative to series lagoons for treatment of industrial waste streams is the Deep Shaft. It is both land conserving and applicable to a wide variety of flow rates. Deep Shaft technology has been found to be average or better than average according to all cost criteria except construction costs and cost per unit of waste removed. The additional construction costs over other conventional technologies are primarily due to the requirements for shaft drilling and lining. Nevertheless, the slightly higher initial capital investments tend to be offset by lower annual and recurring costs such as maintenance, supervision and labor, and chemical and energy costs.

The higher estimate for cost per unit of waste removed is based upon limited information about the application of Deep Shaft technologies to recalcitrant organic materials. The technology is relatively new and cost information was available only for a smaller scale plant treating a highly variable flow. Section IV shows the cost of waste constituent removal expressed as kg of BOD to be \$2.6 (\$26/lb), compared to \$0.11 (\$0.11/lb) for series lagoons and \$0.55 (\$0.55/lb) and \$0.22 (\$0.22/lb) for the studied UNOX and activated sludge facilities, respectively. Based on the economic criteria, the removal cost for future, full-scale Deep Shaft applications will probably approach $0.13/kg ($0.13/lb) of BOD.

Another observation which can be drawn from the economic comparisons is that both of the innovative technologies, Deep Shaft aeration and pure oxygen aeration, compete favorably with the more widely applied conventional activated sludge systems. This would indicate that as these new technologies are developed and additional information is available on their applicability to industrial waste streams, they will be more widely applied to national waste flows.

RECOMMENDED IMPROVEMENTS FOR BIODEGRADATION OF ORGANIC MATERIALS

A primary objective of this study is to indicate how existing biodegradation systems can be upgraded to improve treatment of organic wastes. Such recommendations are based upon insights derived during this study.

The primary operational and/or design improvements should be aimed at overcoming organic and hydraulic overloadings, improving treatment of specific organic constituents, and/or meeting more stringent treatment requirements (25).

Federal and state government agencies presently require industrial waste treatment facilities, both generator-owned and publically-owned to comply with discharge standards. Although present standards stipulate BOD, COD, TOC, and SS removals, it is possible that in the near future these indicators of organic waste materials may be accompanied by new demands for removal of specific organic constituents. The "priority pollutants" associated with the Consent Decree (26) are presently being analyzed in a variety of industrial discharges so that specific hydrocarbon and chlorinated organic solvent discharges to the environment can be controlled.

Increased hydraulic and organic loadings or sudden increases in toxic waste constituents can have a significant impact on the overall efficiencies demonstrated by biological treatment systems. Increased process waste streams or other industrialization associated with treatment plant influents can cause such increases or fluctuations.

Overloads created by industrial contributors can be relieved by pretreatment, by equalization, or by expansion of critical plant components. Equalization of industrial flows by the discharging industry is especially effective when the discharge is concentrated but of relatively short duration (27).

Primary Aerobic Stabilization-Equalization

During the execution of the field study portion of this project, it became evident that industrial influents to biological waste treatment plants were characterized by periodic changes in volume, strength, and composition. All these changes can have a detrimental impact on maintaining desirable biooxidative conditions in the plant. To lessen the chance for system upset, systems should be operated as uniformly as possible. Flow equalization is one means whereby changes in waste quantities and qualities can be dampened and concentrated sludge discharges can be mixed with dilute wastes in some types of storage vessel or basin.

Equalization storage may be located at the site of waste generation, in collection or transfer piping, and at the influent point(s) of the treatment system. Equalization basins have not been fully applied in industrial wastewater collection systems and represent a great potential for improving the quality of contributor-treatment networks and enhancing overall treatment. Specially designed subsurface equalization basins with lift stations may be installed at key points along the collection system and preceded by bar screens and a grit chamber to avoid solids accumulation. Such basins can also be installed at the treatment plant, minimizing head loss and making use of existing pretreatment facilities. Facilities should be provided at equalization basins for periodic removal of settled solids.

It should be noted that flow equalization systems also increase the total volume of the collection and treatment system. Substantial increases in retention time, in turn, will allow for more complete biodegradation of recalcitrant organic materials. To maximize the opportunity for biological stabilization in the equalization basin, it is advisable to provide oxygen and bacterial seed. Aeration of raw influents and contact with activated sludge from downstream processes would provide such an environment. The impact of generated biological flocs from the stabilization basin on primary settling characteristics needs to be studied further.

Another method of providing flow equalization and biological "roughing" treatment prior to the main treatment works is to install a small deep shaft aeration facility between the pretreatment works (e.g., bar screen, grit chamber, and comminutor) and the primary facility. Primary settling would then be best achieved by an air flotation unit with surface and bottom sludge rakes. Figure 57 shows two conceptual industrial waste treatment systems utilizing primary aerobic equalization-stabilization units.

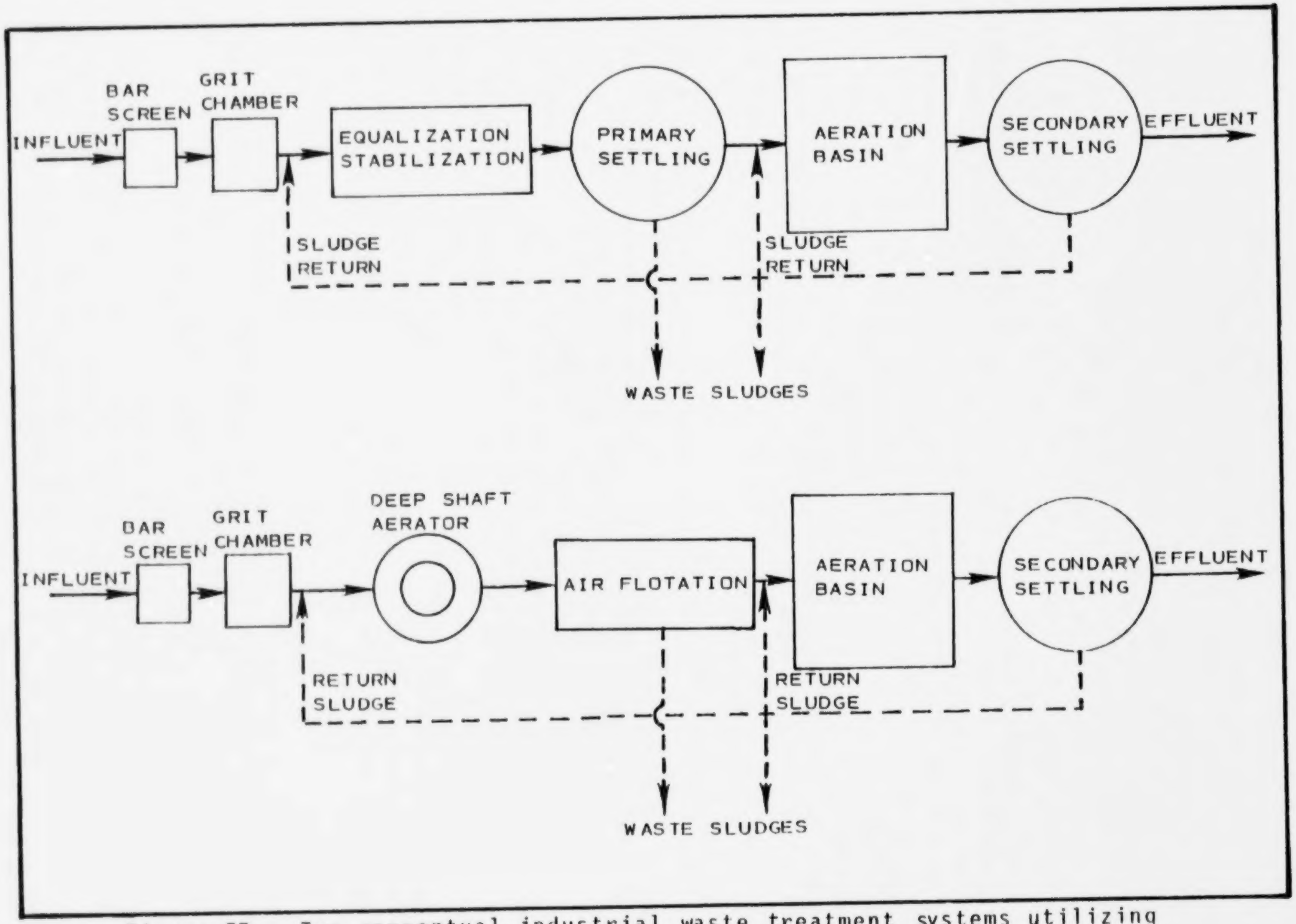
BAR SCREEN
GRIT CHAMBER
INFLUENT
EQUALIZATION STABILIZATION
PRIMARY SETTLING
AERATION BASIN
SECONDARY SETTLING
EFFLUENT
SLUDGE RETURN
SLUDGE RETURN
WASTE SLUDGES
DEEP SHAFT AERATOR
BAR SCREEN
GRIT CHAMBER
INFLUENT
AIR FLOTATION
AERATION BASIN
SECONDARY SETTLING
EFFLUENT
RETURN SLUDGE
RETURN SLUDGE
WASTE SLUDGES

Figure 57. Two conceptual industrial waste treatment systems utilizing primary aerobic evaluation stabilization units.

Primary Anaerobic Digestion-Equalization

Primary treatment in anaerobic equalization basins has also been effective in treating petrochemical wastes. Such basins are particularly effective in treating low molecular weight acids and alcohols (28). Odorous sulfur compounds often associated with industrial waste streams can also be stabilized by anaerobic treatment.

Spill Basins

Spill basins serve as special types of equalization basins, accommodating, storing, and treating overflow volumes of concentrated sludges in the treatment plant influents. Since spill basins are not on-line with the continuous waste flow, special overflow weir or sensor-actuated flow gates must be provided for temporary diversion of flows to the basin structure. In cases where the basin is to be used for hydraulic equalization only, some types of overflow structure is required. Where the basin is used for protecting the on-line biological treatment processes, some method must be provided for anticipating qualitative changes so that the volume which must be diverted before the normal treatment scheme can be restored.

Typically, spill basins are used at industrial waste treatment facilities when there has been an unexpected discharge fluctuation at one of the waste contributors. Such changes can be caused by in-plant spills, improper process control, or irregular activities such as system shutdowns, vessel washings, or purging of in-house storage tanks. Usually, when these occurrences result in irregular waste discharges, plant personnel will immediately warn the treatment plant operator to expect a change in influent characteristics. Such a system usually provides enough lead time to divert the waste stream to the equalization basin and avoid system upsets. Nevertheless, in-stream monitoring devices for detecting radical changes in organic waste concentrations should be developed and used at key points in industrial waste collection systems to alert plant operators to potential overloadings.

Once a volume of waste is diverted to the spill basin, it must be biologically and/or chemically stabilized and then introduced slowly into the regular treatment plant flow. In extreme cases, spill basins are emptied by vacuum truck, and wastes are transported to special off-site disposal facilities.

The cost of equalization-stabilization on spill basin systems will vary considerably, depending on volume requirements, construction methods, and auxiliary equipment such as piping, aerators, liners, land costs, and pumping requirements. Capital costs for equalization facilities have been estimated by various authors and are shown in Table 112.

TABLE 112. COST OF EQUALIZATION FACILITIES (27)*

Basin Size (MG)	Earthen Basin†		Concrete Basin	
	with pumping	without pumping	with pumping	without pumping
0.32	$ 165,000	$ 96,000	$ 223,000	$ 165,000
0.88	226,000	112,000	443,000	329,000
2.40	423,000	178,000	1,037,000	792,000

* All costs updated to 1977 dollars from 1974 (10 percent interest).

† The construction cost for the earthen equalization basin includes excavation, plastic liner, sand subbase, concrete screen pad, dike fill, underdrain, and floating aerator.

Neutralization

The acidity or alkalinity (pH) of the waste stream introduced to the bioreactor must be maintained within a specific range if microbial populations are to be favored. To accomplish this, different industrial waste streams may be selected for treatment based on their neutralizing effects, or chemicals may be purchased and added to the influent wastes. In the former situation, lower operational costs are realized (no chemicals must be purchased), but maintaining the desired pH depends upon the regular flows of each component stream. The stockpiling of chemicals such as sulphuric acid, caustic soda or lime will increase chemical costs but will also provide the capability for adjusting chemical additions based on variations in waste stream characteristics. A relatively sophisticated control system can be applied if the variability is high (74, 97). Neutralization of highly concentrated waste streams may be most effectively achieved before they are mixed with other, more dilute waste streams. Design of an industrial waste treatment facility should include a careful evaluation of all influent waste streams to determine the most cost-effective and reliable method for pH control.

Nutrient Addition

The addition of nutrients required by microbes for efficient biooxidation of carbonaceous substrates was found to be a valuable technique for enhancing treatment efficiency. Many petrochemical, textile, and other industrial wastes are deficient in nitrogen and phosphorus and must be supplemented if biodegradation is to be the primary method of treatment. The advisable carbon-to-nitrogen-to-phosphorus (C:N:P) ratio for aerobic bioconversion is approximately 100:10:1.

Nutrient deficiencies may be overcome in the same manner as discussed for pH control: by chemical addition or by careful selection of influent contributors to ensure a proper balance. As shown in Section IV, major industrial treatment facilities have realized large savings in chemical costs by combining nutrient-deficient waste streams with others having high concentrations of phosphorus compounds or ammonia. The inclusion of a municipal waste stream in industrial influents is another valuable method of providing these materials.

Bacterial Seeding

The maintenance of specially adapted populations of microorganisms by initial or continuous seeding with specially prepared cultures has not played a significant role in enhancing the treatment efficiency of industrial waste treatment plants. The microbial populations of such treatment systems are highly varied and are controlled, in part, by environmental conditions established by plant design, waste characteristics, operational techniques, and competing biota in the same regions of the plant. The presence of a homogeneous culture not directly favored by all these conditions can only be maintained through constant addition of cultures prepared outside the treatment plant environment. This maintenance of an artificial population is usually expensive and of doubtful effectiveness. Biological seed from municipal waste treatment facilities will usually contain all microbial species necessary for biodegradation of a wide variety of industrial wastes.

Extensive Aeration

Aeration of industrial wastes is an important technique in enhancing biodegradation of organic constituents. However, oxygen transfer is only of secondary importance in treating recalcitrant wastes with low rate constant (k) values. Some wastes, such as oils and alcohols, will only be degraded after long periods of contact with activated sludge. This appears to be due to the competition of these materials with more readily degradable organic compounds and requirements for development of special enzymes by some microorganisms before metabolism can be initiated. A long retention time such as that provided by equalization or spill basins must be coupled with efficient oxygen transfer into the waste materials.

Activated Carbon

Activated carbon may be used either in column filtration units or as a powder added directly to the bioreactor to adsorb certain organic materials and provide a concentrating substrate for microbiological activity. In certain cases, such practices may effectively remove toxic components not readily treated biologically and may reduce the need for retaining entire waste volumes for extended periods of time.

It has been noted that there are few current applications of this promising technology (27). Experience has shown that typical treatment costs for activated carbon addition can vary from 0.4 to 1.8 cents/1,100 ℓ. Research and development should be continued in order to increase the regenerative capacity for spent powered carbon.

Temperature Control

Many industrial waste streams, particularly those from petrochemical or kraft mill processes, may reach the treatment facility at elevated temperatures. If these wastes are not cooled to at least 40°C to 45°C, they may adversely affect the microorganisms in the bioreactor.

The use of cooling towers should be considered as an effective means of enhancing stable biodegradation and favoring diverse microbial populations.

Other Pretreatment Techniques

Other pretreatment techniques may also be practiced in order to enhance the biodegradation of problematic organic waste streams. Most of these are physical/chemical treatment processes and are outside the context of biodegradation. Nevertheless, their use in conjunction with biological treatment can greatly improve the overall treatment capabilities.

The pretreatment technologies may be applied to wastes prior to their introduction to the biological treatment processes to eliminate or reduce the total loading of carbonaceous materials. Some technologies, such as solvent extraction, are best applied to single-process waste streams before they are discharged into the industrial collection system for transport to the plant. Other techniques applicable to single or mixed waste flows include reverse osmosis, chemical precipitation, evaporation, ion exchange, distillation, resin adsorption, and density separation. Additional research should be conducted to determine how these treatment techniques may be used in association with biological treatment to provide required effluent qualities.

SECTION VII
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APPENDIX B

SAMPLING AND ANALYSIS: PARAMETER AND STATION SELECTION

SELECTION OF ORGANIC TOXINS FOR SAMPLING AND ANALYSIS

The method of selecting candidate organic constituents for quantitative analysis for each site is shown in Figure B-1. Information from previous industrial surveys was tested according to the selection criteria, and a list of potential organic waste stream constituents was developed (113). Table B-1 is a list of waste products developed for the petrochemical industry.

Once such lists were developed for each of the industrial contributors, specific hazardous organic compounds were identified and their toxicity determined from appropriate literature (104, 113, 119, 129). The resulting candidate hazardous organic waste stream constituents for each site are shown in Table B-2.

The compounds marked with an asterisk (*) in this table were selected as candidates for sampling and quantitative analysis because they are slightly or moderately soluble in water and are potential water contaminants. In addition, these compounds may be analyzed with gas-liquid chromatography on either a polar or nonpolar column system. Ethers, aldehydes, glycols, acids, and nitriles without alpha-H atoms were excluded because of their relatively low toxicity and intermediate or extreme polar characteristics. Analysis of such materials would require additional retooling of the gas chromatograph, adding significantly to the cost of the tests.

Table B-3 shows the classes of compounds considered for final selection. Again, most "polar" and "intermediate polar" classes were excluded for the sake of ease of analysis. Table B-4 shows the 20 compounds finally selected and their designation as either "polar" or "low or nonpolar."

In addition to the 20 organic compounds quantitatively analyzed by gas chromatography, 109 organic compounds were analyzed for their occurrence in the waste stream by gas chromatography/mass spectrophotometry (GC/MS). These organics are shown in Table B-5.

SELECTION OF BIOLOGICAL PARAMETERS FOR ANALYSIS

Microorganisms, bacteria, fungi, algae, protozoa, and viruses can be present in wastewater. Moreover, representatives of all but the viruses are capable of proliferating in wastewater. According to classical ecological theory, a mixture of a wide

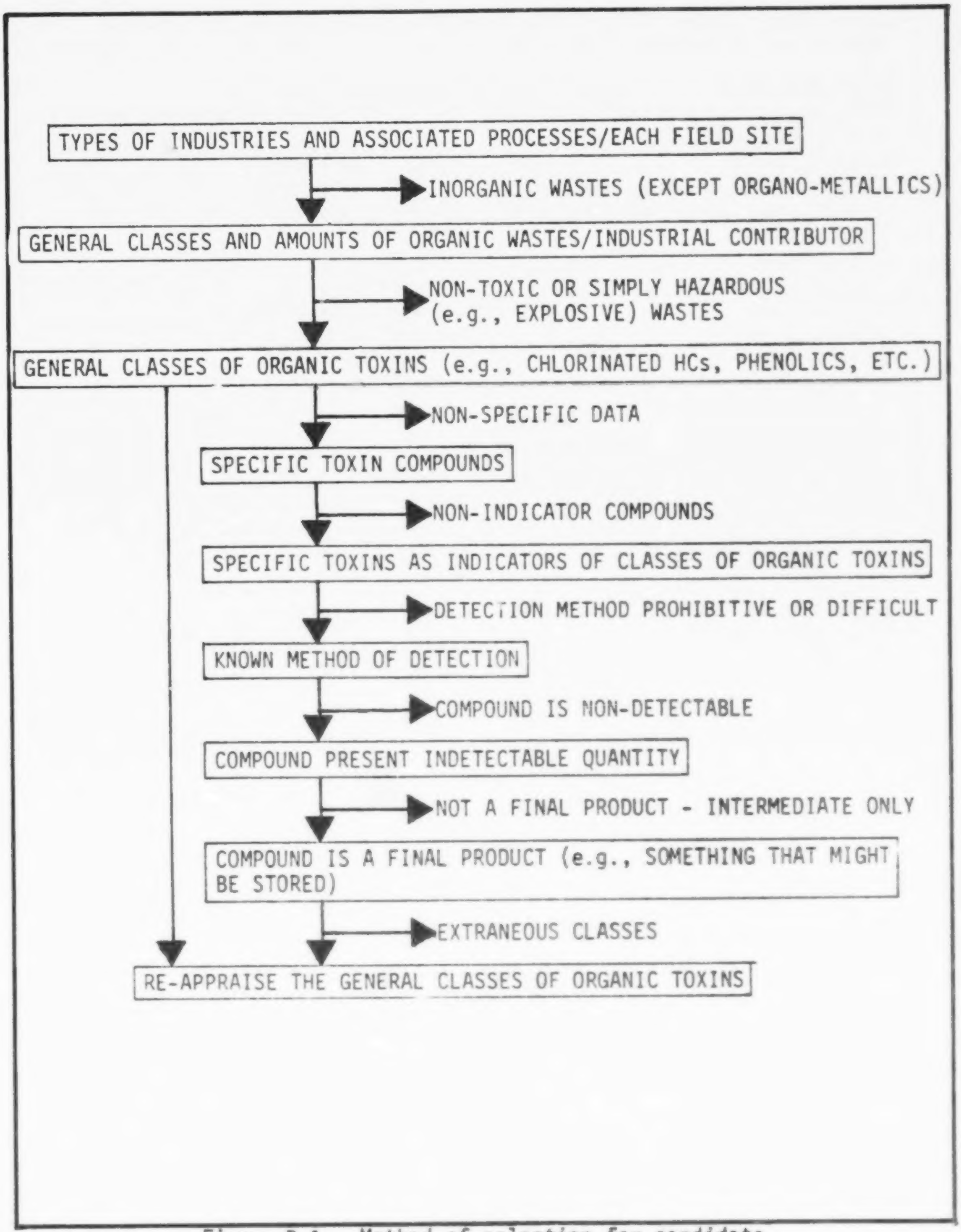

TYPES OF INDUSTRIES AND ASSOCIATED PROCESSES/EACH FIELD SITE
INORGANIC WASTES (EXCEPT ORGANO-METALLICS)
GENERAL CLASSES AND AMOUNTS OF ORGANIC WASTES/INDUSTRIAL CONTRIBUTOR
NON-TOXIC OR SIMPLY HAZARDOUS (e.g., EXPLOSIVE) WASTES
GENERAL CLASSES OF ORGANIC TOXINS (e.g., CHLORINATED HCs, PHENOLICS, ETC.)
NON-SPECIFIC DATA
SPECIFIC TOXIN COMPOUNDS
NON-INDICATOR COMPOUNDS
SPECIFIC TOXINS AS INDICATORS OF CLASSES OF ORGANIC TOXINS
DETECTION METHOD PROHIBITIVE OR DIFFICULT
KNOWN METHOD OF DETECTION
COMPOUND IS NON-DETECTABLE
COMPOUND PRESENT INDETECTABLE QUANTITY
NOT A FINAL PRODUCT - INTERMEDIATE ONLY
COMPOUND IS A FINAL PRODUCT (e.g., SOMETHING THAT MIGHT BE STORED)
EXTRANEOUS CLASSES
RE-APPRAISE THE GENERAL CLASSES OF ORGANIC TOXINS

Figure B-1. Method of selection for candidate organic constituents for analysis.

TABLE B-1. POTENTIAL PETROCHEMICAL WASTE PRODUCTS

Cyclohexanol
Toluene 2,4-diamine
Acetaldehyde
Acetic acid
Acetic acid salts; copper acetate; potassium; zinc
Acetone
Acetylene
Acrylonitrile
Butanol-N
Butanol-sec
Carbon tetrachloride
Chloroform
Diethylamine
Ethanol (28695)
Ethylene
Ethylenediamine
Ethyleneimine
Ethyl chloride
Ethylene dichloride
Ethylene glycol
Ethylene glycol diacetate
Ethylene oxide
Formaldehyde
Formic acid
Formic acid, sodium salt (sodium formate)
Glutamates
Glycol ethers
Hexanediamine (1.6-hexamethylenediamine)
Isopropyl ether
Methanol
Methylamines
Methylene chloride
Methyl chloromethylether
Methyl acetate
Methyl chloride
Methyl ethyl ketone
Methyl isobutyl ketone
Methyl methacrylate
Propylene
Propylene chloride
Propylene glycol
Propylene oxide
Vinyl acetate monomer
Vinyl chloride monomer
Xylene propanol

TABLE B-2. CANDIDATE ORGANIC TOXIC CONSTITUENTS FOR FIELD SAMPLING AND LABORATORY ANALYSIS

Washburn Tunnel Facility	40-Acre Facility	Deep Shaft Paris, Ont.
benzene*	benzene*	benzene*
phenol*	phenol*	phenol*
cresol*	ethyl benzene*	toluene*
toluene*	styrene*	butanol*
xylene*	butanol*	ethylene dichloride*
xylenol*	ethylene dichloride*	methanol*
hexanol*	hexanol*	isopropanol*
acrylonitrile*	methanol*	acetonitrile
ethylene glycol diacetate	n-and isopentanol*	ethylene glycol monomethyl ether
formaldehyde	n-and isopropanol*	carbon tetrachloride*
formic acid		formaldehyde
methanol*		various proprietary dyes*
methyl acetate		
methyl chloride*		
methyl methacrylate		
carbon tetrachloride*		
butyl mercaptan*		
ethyl mercaptan*		
methyl mercaptan*		

TABLE B-3. GENERAL CLASSES OF ORGANIC TOXINS FOR ANALYSIS IN FIELD SAMPLES

Polarity	Class	# of Compounds per Class	
Most polar	glycols	1	
	acids	3	4
Polar	alcohols	7	
	phenols	3	
	nitriles with alpha-H atoms	1	11
Intermediate polar	ether	1	
	nitriles without -H atoms	1	
	aldehyde	1	3
Low polarity	CH_3Cl	1	
	CH_2ClCH_2Cl	1	
	aromatic hydrocarbons	5	7
Non-polar	mercaptans	3	
	CCl_4	1	4
	other chlorinated HC's		

TABLE B-4. FINAL LIST OF CONSTITUENTS FOR ANALYSIS AT THE FOUR FIELD SITES

Washburn Tunnel Facility	Group*	40-Acre Facility	Group*	Deep Shaft Paris, Ont.	Group*
Benzene	2	Benzene	2	Benzene	2
Phenol	1	Phenol	1	Phenol	1
Cresol	1	Ethyl benzene	2	Toluene	2
Toluene	2	Styrene	2	Butanol	1
Xylene	2	Butanol	1	Ethylene dichloride	2
Xylenol	1	Ethylene dichloride	2	Methanol	1
hexanol	1	Hexanol	1	Isopropanol	1
Acrylonitrile	1	Methanol	1	Carbon tetrachloride	2
Methanol	1	n-and iso-petanol	1		
Methyl chloride	2	n-and iso-propanol	1		
Carbon tetrachloride	2				
Butyl mercaptan	2				
Ethyl mercaptan	2				
Methyl mercaptan	2				

* 1 = Polar compounds
2 = Low or non-polar compounds

TABLE B-5. LIST OF ORGANICS ANALYZED BY GC/MS

I. PESTICIDES

Acrolein
Aldrin
-BHC
-BHC
-BHC (Lindane)
-BHC
Chlordane
DDD
DDE
DDT
Dieldrin
-Endosulfan
-Endosulfan
Endosulfan sulfate
Endrin
Endrin aldehyde
Heptachlor
Heptachlor epoxide
Isophorone
TCDD (2,3,7,8-tetrachlorodioenzo-p-dioxin)
Toxaphene

II. PCB's AND RELATED COMPOUNDS

PCB-1016 (Arochlor 1016)
PCB-1221 (Arochlor 1221)
PCB-1232 (Arochlor 1232)
PCB-1242 (Arochlor 1242)
PCB-1248 (Arochlor 1248)
PCB-1254 (Arochlor 1254)
PCB-1260 (Arochlor 1260)
2-Chloronaphthalene

III. HALOGENATED ALIPHATICS

Methane, bromo- (methyl bromide)
Methane, chloro- (methyl chloride)
Methane, dichloro- (methylene chloride)
Methane, chlorodibromo-
Methane, dichlorobromo-
Methane, tribromo- (bromoform)
Methane, trichloro- (chloroform)
Methane, tetrachloro- (carbon tetrachloride)
Methane, trichlorofluoro-
Methane, dichlorodifluoro-

Phenol, 2,4-dinitro-
Phenol, 2,4-dimethyl-
m-Cresol, p-chloro-
o-Cresol, 4,6-dinitro-

VII. PHTHALATE ESTERS

Phthalate, dimethyl-
Phthalate, diethyl-
Phthalate, di-n-butyl-
Phthalate, di-n-octyl-
Phthalate, bis(2-ethylhexyl)-
Phthalate, butyl benzyl-

VIII. POLYCYCLIC AROMATIC HYDROCARBONS

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(ghi)perylene
Benzo(a)pyrene
Chrysene
Dibenzo(a,n)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

IX. NITROSAMINES AND OTHER NITROGEN-CONTAINING COMPOUNDS

Nitrosamine, dimethyl- (DMN)
Nitrosamine, diphenyl-
Nitrosamine, di-n-propyl-
Benzidine
Benzidine, 3,3'-dichloro-
Hydrazine, 1,2-diphenyl-
Acrylonitrile

variety of substrates will support a rich and varied population; conversely, single substrates will, by selective pressure, give rise to a restricted population (3). Studies have presented information on the tremendous diversity of the microbiological flora present in municipal wastewater treatment systems (69), yet similar information for microbial type or number in industrial wastewater treatment is limited (153).

Studies on microbes in industrial treatment systems have reported the predominance of one or a few microbial species (30, 83, 153). These are in agreement with the above premise that the small number of substrates found in industrial wastewater restricts the diversity of the microbial population. The microbiological portion of this study was designed to test this premise at the treatment facilities surveyed and determine which, if any, microbial group predominates and the organic substrates utilized by specific microbes.

STATION SELECTION AND SAMPLING FREQUENCY

Both the location of sampling stations and sampling frequency were chosen to aid in characterizing biological treatment of hazardous organic materials. In general, sampling stations within the treatment systems were selected to indicate the changes in the waste streams as they pass through the unit treatment processes and are discharged to the receiving environment.

Sediment sampling sites at and adjacent to the treatment facilities outfalls were selected to detect either the presence or accumulation of organic compounds. These sites were located with an understanding of the receiving body hydrology in relation to net flow (drainage of uplands) and cyclic effects of tidal currents. These relationships were used to estimate the maximum upstream displacement of constituents from the outfall. The control sediment sampling sites were located just upstream of that point. Figure B-2 is a schematic of the sediment sampling sites locations.

SAMPLING METHODS

Many factors must be considered in devising a sampling regime which will result in representative samples and meaningful conclusions. Ideally, the influent-effluent and in-plant waste stream characteristics would be constant under such conditions, and the process could be characterized with relatively few replicate samples. However, most contributing industries discharge certain waste materials intermittently and are continuously changing process flows during operation. Furthermore, processes in the waste treatment plant itself can make it difficult to compare effluent constituent levels with known influent values. Changes in operation and efficiencies of the various units and complete mixing in the process flow are major causes of this problem. Figure B-3 shows how one fluctuating constituent in a plant effluent might be affected.

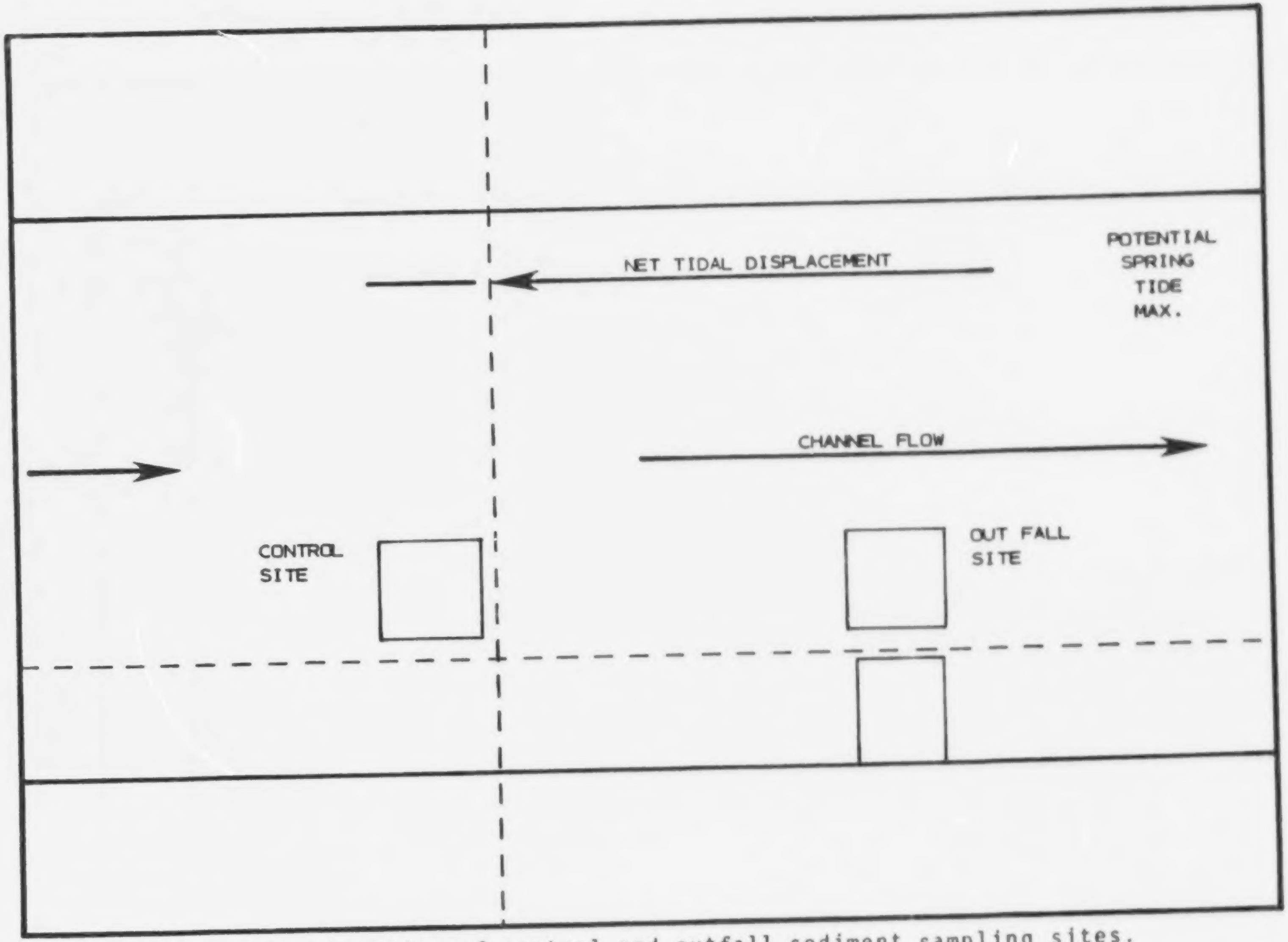

NET TIDAL DISPLACEMENT
POTENTIAL SPRING TIDE MAX.
CHANNEL FLOW
CONTROL SITE
OUT FALL SITE

Figure B-2. Location of control and outfall sediment sampling sites.

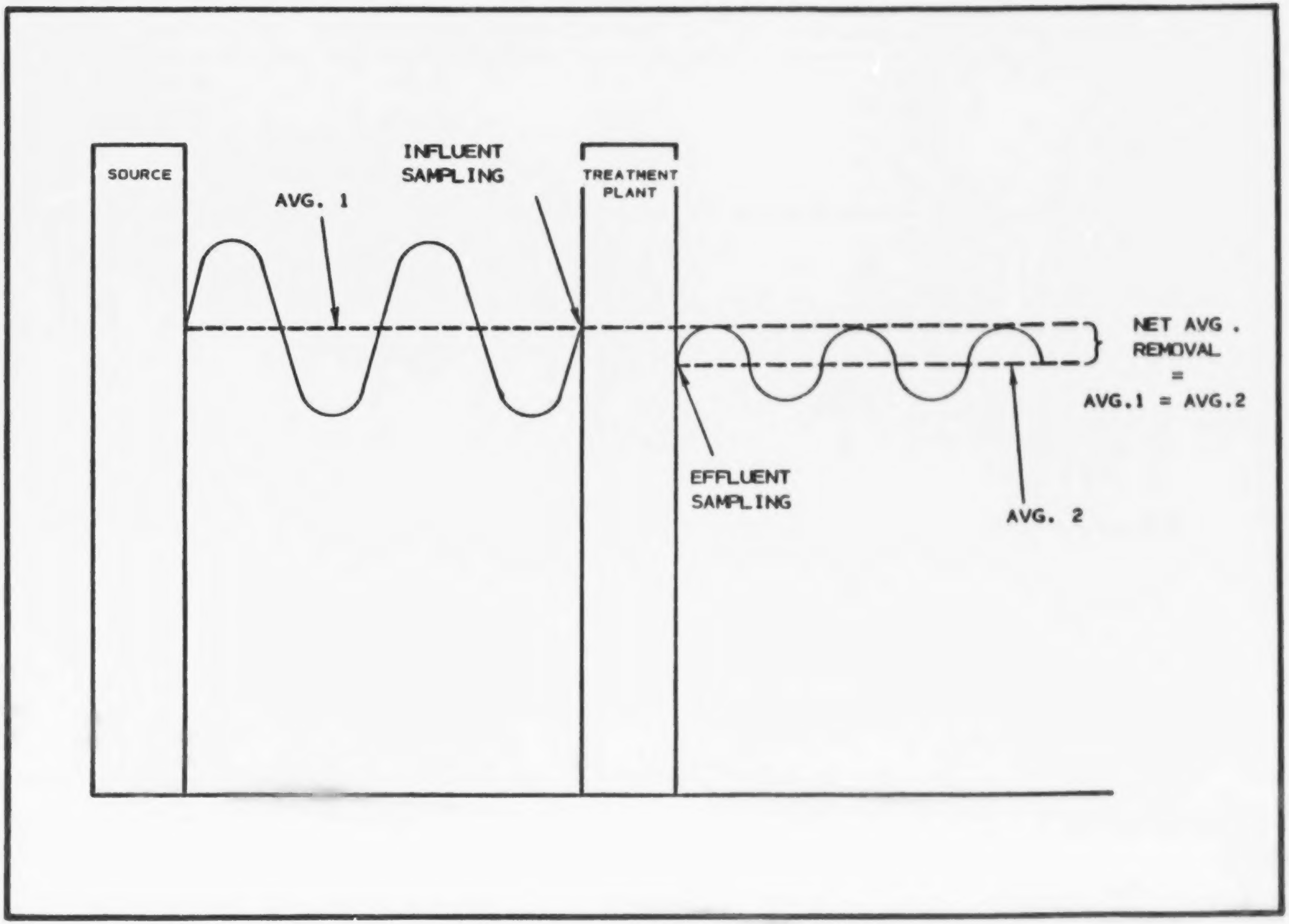

SOURCE
INFLUENT SAMPLING
AVG. 1
TREATMENT PLANT
NET AVG. REMOVAL = AVG.1 = AVG.2
EFFLUENT SAMPLING
AVG. 2

Figure B-3. Hypothetical fluctuation of one constituent in-plant influent-effluent.

In sampling waste streams, there are certain variables which must be considered in identifying various trace organic constituents. Independent variables are:

- Changes in industrial discharges
- Changes in plant operations/efficiencies
- Treatment plant retention time.

Dependent variables are:

- Rate of sampling (e.g., 1/hr, 12/day, 1/day)
- Duration of sampling period (e.g., 1 day, 1 wk, 2 wk).

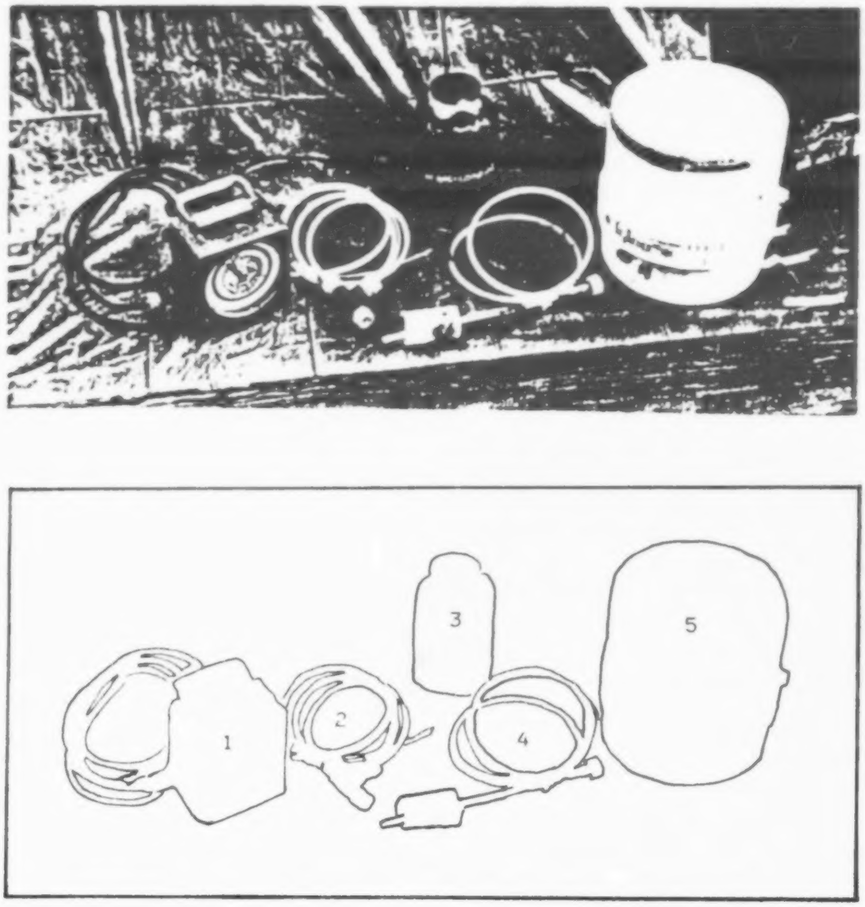
In systems such as wastewater treatment plants, independent variables fluctuate to such an extent that characterization of the waste stream constituents by a few replicate samples is meaningless. Therefore, the best estimate of a waste constituent average value can be found by controlling the dependent variables and taking numerous small composite samples over an extended length of time. Although many of the specific details concerning hourly, daily, or weekly fluctuations may be lost, composite sampling greatly reduces the number of analyses and amount of labor involved as compared to numerous individual grab samples. However, where composite sampling was not feasible, e.g., sampling sludge from secondary clarifiers with fluctuating sludge blanket heights, grab sampling was used.

Composite Sampling

For a representative determination of trace organics in industrial waste streams, provisions must be made for restricting biodegradation of the organic compounds before analyses can be performed. The most popular procedure for stopping biodegradation during composite sampling is refrigeration of the sample. This principle was incorporated into the composite sampler design through immersion of the sample in an ice bath within an insulated container. With this setup, the sample temperature was maintained at 3°C to 5°C during the duration of the composite sampling periods.

Figure B-4 shows the composite sampler equipment. Plate 1 is a close-up view of the equipment in operation at a field location. The composite sampler pump flow is 4 ℓ/min. A T-fitting allowed for draw-off of a portion of the sampler flow to a brown glass bottle in the insulated cooler. The composite samplers were set up to draw 4 aliquots of approximately 35 mℓ each per hr. This gave a 24-hr sample volume of 3.36 ℓ.

Care was taken to ensure continuous composite sampling, even during periods of low flow, by using a sampler influent tubing long enough to remain immersed in the waste stream. Sampling



1. SURVEYOR AUTOMATIC COMPOSITE SAMPLER
   110V N-CON SYSTEMS CO.

2. SAMPLER EFFLUENT TUBING (0.6 cm I.D.
   POLYETHYLENE) WITH T-FITTING AND 0.3 cm
   I.D. DRAW OFF TUBING TO SAMPLE BOTTLE

3. 3.8 LITER BROWN GLASS BOTTLE, HEXANE
   WASHED

4. SAMPLER INFLUENT TUBING (0.6 cm I.D.
   POLYETHYLENE) 0.45 KG WEIGHT AT ONE END

5. 11.4 LITER PLASTIC INSULATED COOLER

Figure B-4. Composite sampler equipment.

points were located in areas of turbulence to ensure representative completely mixed samples. Samples were removed daily, and the ice bath replenished.

Grab Sampling

The sampling schedule necessitates frequent grab sampling at different locations. A sampler which required cleaning after each use, e.g., a Van Dorn Bottle, could not be used. Therefore, a grab sampler was devised which would allow rapid, repeated sampling of wastewater without repeated washing. The grab sampler consists of a sampler body with attached nylon rope line and was constructed of 10.2-cm (4-in) diameter polyvinyl chloride pipe (PVC) and pipe caps (Figure B-5). One end was threaded for easy removal of the pipe cap. Thus, clean sample bottles could be inserted into the sampler quickly and filled directly by lowering into the waste stream. A stopper with an attached line and necessary ballast was used when samples were taken at various depths in the wastewater stream. The grab sampler is 215.4 cm (10 in) long and weighs 3.2 kg.

Sediment Sampler

A La Motte Bottom Sampling Dredge was used to obtain samples of bottom sediment. The dredge is 20 cm (7 in) long, 7 cm (2.75 in) in diameter, and retrieves a sample volume of 0.77 ℓ.

SAMPLE TRANSPORTATION AND PRESERVATION

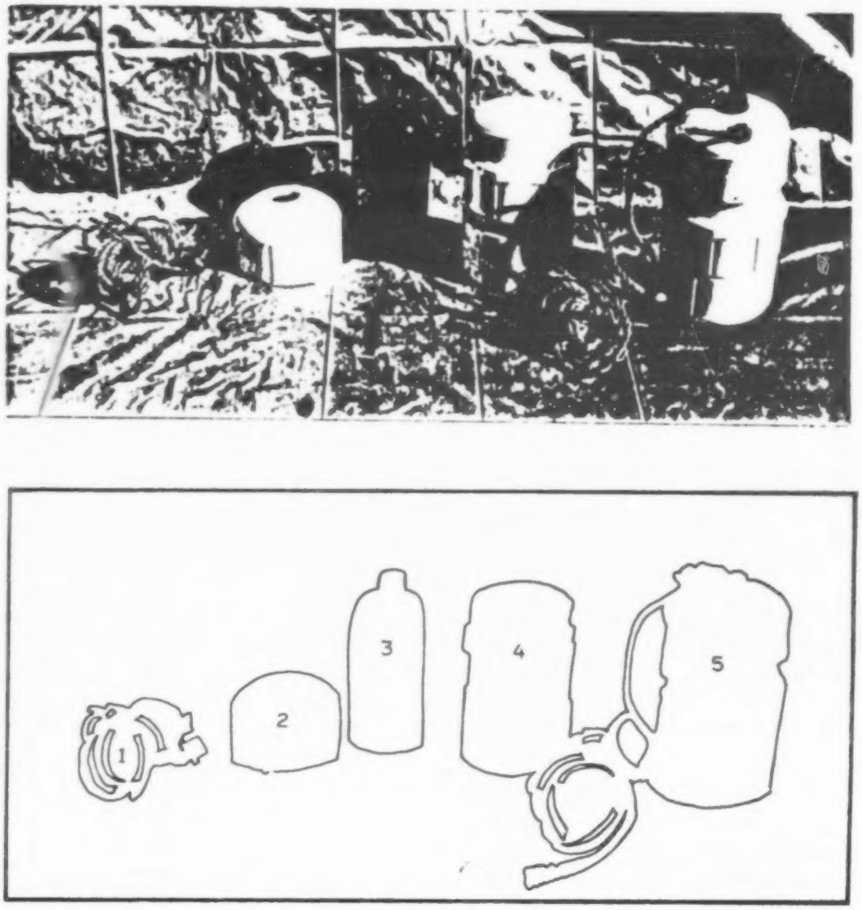
Two types of containers were used to hold the samples for storage and shipment. One-liter brown glass jars were used for the organic analysis samples, while biological samples were stored and shipped in one-liter polyethylene cubitainers.

All samples were shipped in ice and packed in insulated containers.

ANALYTICAL METHODS

Chemical Analysis

The organic analyses by gas chromatography (GC) and gas chromatography/mass spectrometer (CG/MS) were completed essentially according to the procedure described in the EPA protocol for sampling and analysis of industrial effluents (158). For analyses of organic compounds not covered by EPA protocol, the samples were extracted at pH 11, then pH 2. Each of the extracts were then combined and concentrated in a Kuderna-Danish (K-D) evaporation apparatus. The concentrated extract was then injected into a gas chromatograph unit equipped with a flame ionization detector (GC-FID). The same analytical parameters were used as specified for the Protocol base/neutral fraction analysis.



1. HARD RUBBER STOPPER WITH ATTACHED NYLON LINE

2. THREADED PIPE CAP, PVC, 10.2 cm DIAMETER

3. 1 LITER BROWN GLASS BOTTLE, HEXANE WASHED

4. COMPOSITE SAMPLER BODY, PVC, 10.2 cm DIAMETER, 19 cm LENGTH

5. COMPLETE GRAB SAMPLER UNIT WITH ATTACHED NYLON LINE

Figure B-5. Grab sampler equipment.

In the VOA procedure, the Bellar and Lichtenberg hardware was employed. Instead of interfacing this hardware with the GC/MS, the syringe was inserted into the septum of the gas chromatograph. Conditions were otherwise in accordance with EPA Protocol. As in the semivolatile analyses, assignments were made on the basis of single-column retention volumes.

Analysis of purgeables in sediment samples was conducted in accordance with the technical intent of EPA's "Chemistry Laboratory Manual/Bottom Sediments." Although this manual does not treat the VOA subject, it specifies analysis of organics in the "standard elutriate," or water analytically brought into contact with the sediment sample. This was done by adding a measured volume of water to furnish an ullage-free supernatant over about an equal volume of sediment contained in a centrifuge tube. A septum was then afixed and the tubes shaken for 30 min. Following this, the tube was centrifuged and the supernatant tested in the usual EPA Protocol manner.

Sludge samples, containing only a low level of solids, were handled as liquids. Although the solids contents were determined, constituent levels have been expressed on a weight/volume basis.

Microbiological Analysis

Microbiological analyses of the biological sludges from the studied treatment facilities were undertaken to identify the general groups of microbes present, the relative concentration of microbes, and the growth of isolated microbes on selected carbon source media.

Wet mounts and gram-stain smears were prepared upon receipt of the samples at the laboratory. Following complete mixing of the samples to disperse solids, dilutions were prepared in 0.01-percent peptone water blanks. Aliquots were then taken for Most Probable Number (MPN) determinations and for plate counts. For the MPN procedure Standard Methods, lactose broth was employed (10 mℓ/tube plus a durham tube). One-milliliter samples of the dilutions were introduced and the tubes were incubated at 35°. Gas formation was observed in accordance to the recommended procedure (148).

MPN results are in terms of estimated total coliform population. Gas positive tubes were subcultured to eosin-methylene blue (EMB) agar and held for 24 hr at 35°C. Subsequent observation of the EMB plates was done to identify typical colonies (*Escherichia coli*, Enterobacter, possibly Salmonella or Shigella, etc.).

Plate counts were determined using Standard Methods Agar (10) with two plates per dilution. Total plate counts were reported in terms of 5 days incubation at 24°C. Representative colonies were picked and maintained on slants under refrigeration for later determination of carbon source utilization. The existence of an autotrophic microbe (sulfur-iron oxidizing bacteria) was confirmed by inoculation of thiosulfate-mineral salts medium and ferrous iron-mineral salts medium.